# Thermal Characteristics of Lignin Residue from Industrial Processes

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Many pulp mills and biorefineries today are focusing on the utilization of their residual lignin for economic return. Although lignin can be burned to produce energy, it also has the potential for the production of value-added products. Technical lignins have modified structure and contain different impurities, which depend on the original material, as well as the extraction process. Among the various techniques for lignin extraction, kraft and steam explosion processes are the most commonly used in the pulping and biorefinery industries, respectively. The objective of this work was to compare the thermal behavior of industrial lignins produced from kraft pulping and steam explosion, with that of their chemically extracted, purified forms. It was found that the purified lignins have very similar thermal properties to one another, while impurities in the industrial lignins significantly alter their thermal behavior, and hence their potential in value-added applications. The percentage of degradation from 200 to 600 °C and glass transition temperature of original steam-exploded lignin was 68.5% and 149.16 °C, while of original kraft lignin was 26.0% and 109.82 °C. These values were altered after purification to 61.0% and 158.99 °C for steam-exploded lignin; and to 40.0% and 129.82 °C for kraft lignin, respectively.

*Keywords: Industrial lignins; Impurities; Thermal behavior; Glass transition temperature; XRD; EDS*

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## INTRODUCTION

Lignin is one of the most abundant natural substances in the world, and it is produced as a by-product in pulp mills and cellulosic ethanol biorefineries. Although the major portion of lignin is burned to produce energy in recovery boilers (Mohan *et al.* 2006), there is potential to utilize it in higher-value applications (Vishtal and Kraslawski 2011). The use of lignin is limited for value-added products due to its high content of impurities, which are generated during the extraction process. Methods exist for the purification of lignin; however, these processes add cost and complexity to the lignin recovery process. Recently, isolated lignin has been used for conversion into value-added products, such as phenolic resins (Alonso *et al.* 2004; Khan *et al.* 2004; Sarkar and Adhikari 2001; Tejado *et al.* 2007), carbon fiber (Schmidl 1992; Kadla *et al.* 2002), and polymer blends (Cazacu *et al.* 2004; Gosselink *et al.* 2004b; Kadla *et al.* 2002). Therefore, it is of interest to understand the differences between various industrial lignins as they are generated by their original extraction process as compared to their purified form.

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Technical lignins are different from each other to a significant extent because they originate from different sources and separation processes such as kraft, soda, steam explosion, organosolv, and hydrolysis (Vishtal and Kraslawski 2011). The kraft process is a prominent method for making pulp and produces the largest volume of lignin. In this process, *α*-aryl and *β*-aryl ether bonds in lignin are cleaved by alkaline hydrolysis (in a mixture of sodium hydroxide and sodium sulfide) in which 90% of the lignin is removed before the bleaching process (Chakar and Ragauskas 2004). The generated aqueous solution, which is called black liquor, contains ligneous material (30 to 45 wt. %), saccharinic acids (25 to 35 wt. %), formic and acetic acid (10 wt. %), extractives (3 to 5 wt. %), sodium (17 to 20 wt. %), and sulfur (3 to 5 wt. %) (Wallberg *et al.* 2003). In the steam explosion process, biomass is fractionated for producing cellulosic ethanol (Doherty *et al.* 2011). In the pretreatment step of the process, biomass is exposed to pressurized steam, followed by depressurization. This rapid change in pressure results in the hydrolysis of the hemicelluloses and the cleavage of lignin-hemicellulose bonds (Li *et al.* 2007). Therefore, the lignocellulosic structure breaks down, and as result, the lignin is partially depolymerized while the hemicellulose can be readily hydrolyzed (Cara *et al.* 2006). The removal of hemicellulose increases the average pore size of the substrate and thus enhances cellulose degradation by making more surface area accessible to enzymes (Hendriks and Zeeman 2009; Taherzadeh and Karimi 2008).

There are a number of methods for isolating lignin from the industrial residue stream. The LignoBoost® process is used to remove lignin from concentrated kraft black liquor by acidifying it with carbon dioxide (Beis *et al.* 2010). When carbon dioxide is absorbed into the alkaline black liquor, the pH is decreased, and the lignin becomes hydrophobic and precipitates. The lignin is then dewatered to 65%, and after filtration, the filter cake is re-dispersed and acidified with sulfuric acid. In another technique (Abacherli and Doppenberg 2001), lignin is precipitated from the black liquor solution by reducing the pH while at room temperature; subsequently, the mixture is heated to about 70 to 80 °C to turn it from a gelatinous form into a filterable form. Lignin is separated by filtration, washed with water, and dried in an oven.

The ash content of herbaceous biomass is much higher than that of wood (which is usually less than 1%) (Pan and Sano 2005). The major elements in wood ash are calcium, potassium, and magnesium, while sodium and silicon are present in relatively smaller amounts (Misra *et al.* 1993). Typically, herbaceous plants contain much higher Si content. For instance, the ash of wheat straw and rice straw contain 9.6% and 16.5% silicon, respectively, while aspen and white oak contain only 0.1% silicon in their ashes (Misra *et al.* 1993; Pan and Sano 2005). However, the source and the amount of minerals in industrial lignins depend more on the extraction process than the plant species. For instance, alkaline pulping processes, such as kraft, produce lignin with high ash content (43.6%), while autohydrolysis (1.2%) and organosolv (0.1%) techniques result in low ash content (Zabaleta 2012). The sources of these minerals can be the various chemicals used in the pulping process or metallic matter entering the process from piping and machinery (Zabaleta 2012).

In this work, lignin was isolated from black liquor and cellulosic ethanol residues to elucidate the differences in behavior of the industrial lignin materials compared to that of their purified forms. The ash content was also analyzed to determine the chemical composition of mineral impurities in the original and isolated lignin.

## EXPERIMENTAL

### Materials

Two industrial lignins and two commercial lignins were used in this study: L1 was derived from a cellulosic ethanol biorefinery, which uses hardwood/herbaceous biomass; L2 was kraft black liquor obtained from a pulp mill in Brazil utilizing eucalypt species. Commercial lignins are L3 and L4. The raw material and extraction method of the four different lignins are presented in Table 1.

**Table 1.** Description of Lignin Samples

| Label | Lignin | Raw material | Industry | Extraction Method |
|-------|--------|--------------|----------|-------------------|
| L1 | Lignocellulosic Biorefinery | Hardwood/ Herbaceous | Cellulosic Ethanol | Steam Explosion |
| L2 | Kraft Black Liquor | Hardwood | Pulp | Kraft |
| L3 | Commercial | Softwood | Pulp | Kraft |
| L4 | Commercial | Herbaceous | Pulp | Soda |

### Lignin Isolation

Lignin samples were isolated using the Abacherli and Doppenberg (2001) method. Briefly, lignin was dissolved in 0.5 M NaOH and filtered with a Büchner funnel with a paper membrane filter (1-µm mesh). Lignin was then precipitated with sulfuric acid to a pH of 2 to 3 and heated to 70 to 80 °C. The resulting precipitate was filtered and subsequently washed several times with water at 50 to 60 °C, followed by washing with water at room temperature. The material was dried at 50 °C overnight (Fig. 1). The purity of each lignin was determined as the weight ratio of the purified lignin to the crude lignin,

$$Purity\ (\%) = (A/B) \times 100 \qquad (1)$$

where $A$ is the mass of purified lignin (oven dried) (g) and $B$ is the mass of crude material (oven dried) (g).
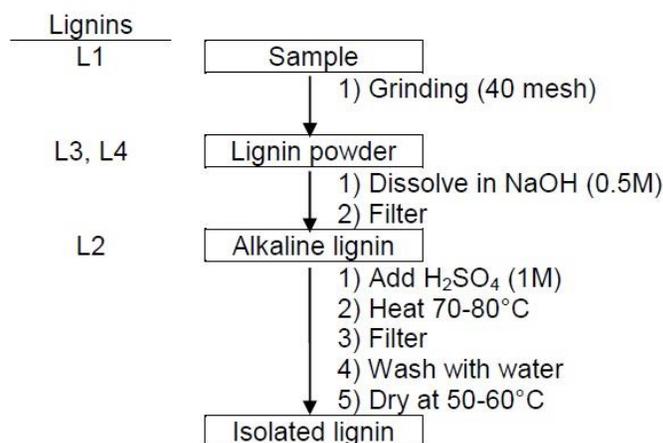


**Fig. 1.** Lignin isolation process

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## Ash Content Determination

The ash content of the samples was gravimetrically determined after incineration at 525 °C or 900 °C (TAPPI method T 211 om-93, 1999). About 0.5 g of moisture-free sample was weighed and placed in a muffle furnace at 525±25 °C (or 900±25 °C) for 4 h. The temperature was increased to 250 °C slowly so that the sample was carbonized without flaming. At the conclusion of heating, samples were placed in a desiccator and cooled to room temperature prior to weighing. Samples were white/gray in color on completion of the heating cycle. Samples were weighed on an analytical balance to the nearest 0.1 mg. The ash content was determined as follows,

$$Ash\ Content\ (\%) = (A/B) \times 100 \tag{2}$$

where $A$ is the mass of ash (g) and $B$ is the mass of the test specimen (oven dried) (g).

## Energy-Dispersive X-Ray Spectroscopy (EDS)

To elucidate the nature of the ash, a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was employed. A thin layer of ash was carefully sprinkled onto double-sided carbon tape mounted on SEM aluminum stubs. All samples were sputter-coated and imaged using a JEOL (JSM-6610LV) scanning electron microscope equipped with a backscattered electron detector in low-vacuum mode (Johnson *et al.* 2010). Each ash sample was characterized by examining all the ash particles observed within the whole image. EDS analysis detects signals from all elements present in the material and provides a qualitative analysis.

## X-ray Diffraction (XRD)

XRD patterns were collected on a Philips (PW1830) diffractometer (40 kV, 40 mA) equipped with a Ni filter, using Cu K$\alpha$ radiation ($\lambda$ =1.54 Å). Scans were performed from 10° to 50° with 0.02° increments at 2 s per step. Identification of chemical compounds was performed using X'Pert Highscore Software (ver. 2.2) and the ICDD database.

## Thermogravimetric Analysis (TGA)

About 12 to 14 mg of lignin sample was weighed into a standard ceramic crucible and placed in a NETZSCH thermogravimetric analyser (Model STA 449F3). Heating was performed from room temperature to 1100 °C at a rate of 10 °C min$^{-1}$. The test was carried out under an argon atmosphere with a flow rate of 20 mL min$^{-1}$. A curve of weight loss against temperature was obtained from the instrument.

## Differential Scanning Calorimetry (DSC)

DSC of lignin samples was performed with a TA instrument-DSC Q200. The results were processed using "Universal 4.2E TA" software. Each sample (2 to 5 mg) was weighed into a standard aluminum pan (40 µL) and heated under a nitrogen atmosphere with a flow rate of 15 mL/min. The sample was initially heated to 200 °C at a heating rate of 10 °C/min. Next, the sample was cooled down to -10 °C with a cooling rate of 30 °C/min. Finally, the sample was reheated to 200 °C with a heating rate of 10 °C/min. The initial heating and cooling cycle was carried out to clear the thermal history of the sample to eliminate the endothermic enthalpy relaxation that usually affects the $T_g$ determination

(Poursorkhabi *et al.* 2013; Rials and Glasser 1984). The $T_g$ value of each sample was measured from the last heating cycle.

## RESULTS AND DISCUSSION

### Lignin Purity

The percentage of isolated lignin from the industrial samples (L1 and L2) can be seen in Table 2, as well as the commercial lignins, which both had very high lignin content (L3: 94.43% and L4: 95.25%). L1 (cellulosic ethanol residue) contained 37.95% lignin. The black liquor (L2) had significantly lower lignin content (27.12%) compared to steam-exploded lignins (L1). The percentage of extracted lignin from the black liquor falls within the expected range of 20 to 40% lignin based on the dry content (Vishtal and Kraslawski 2011).

**Table 2.** Percentage of Isolated Lignins from Alkaline Extraction

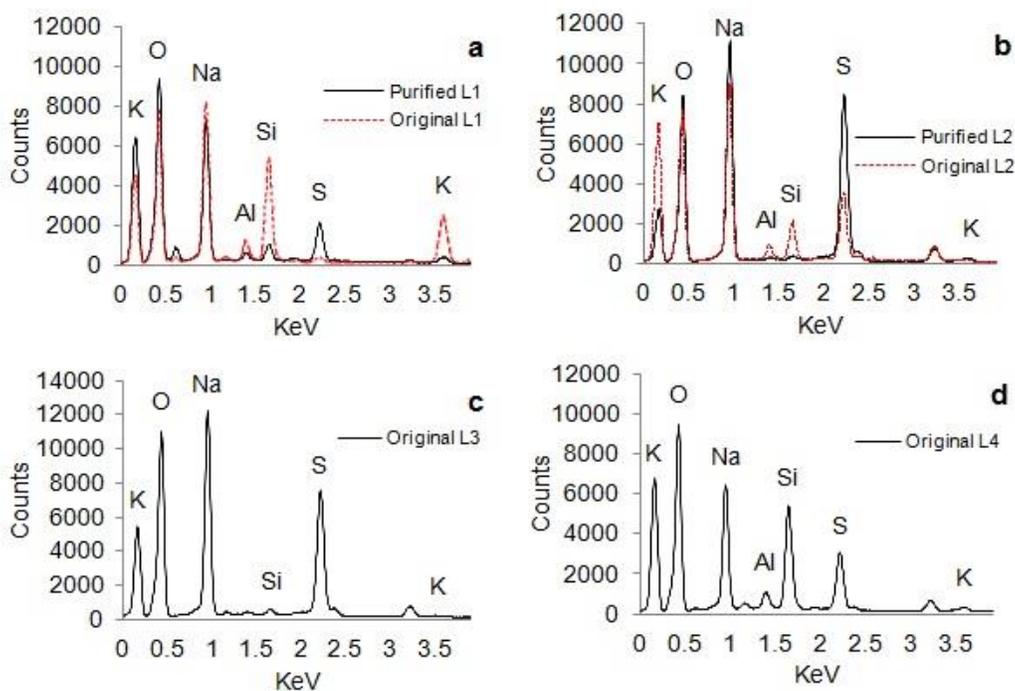| Lignin | Isolated lignin (%) |
|--------|--------------------|
| L1 | 37.95 |
| L2 | 27.12 |
| L3 | 94.43 |
| L4 | 95.25 |

### Ash Analysis

The ash or inorganic content of the original and isolated lignins can be seen in Table 3. The ash content of sample L1 represented a fairly small proportion of the material (2.31%) because the cellulosic ethanol process used steam and enzymes to extract the carbohydrates, which left behind a relatively chemical-free residue. On examination of the EDS spectrum (Fig. 2a), it can be seen that its ash also contained K, Na, Al, S, and silica. Wood in general does not contain silica; therefore, the presence of silica can be attributed to the wheat straw used in the biorefinery process (Table 1). The ash content of wheat straw is much higher than that of wood. The ash content of wood is usually less than 1%, while the ash content of wheat straw is about 9.6%, of which 76% is silica (Pan and Sano 2005). The purified L1 contained 0.45% ash, which was the lowest ash among the purified samples. It has been reported that the lignin produced from organosolv techniques contains 0.1% ash contamination (Zabaleta 2012).

The ash content of L2 was extremely high and represented approximately 36% of the material. This can be attributed to high amounts of sodium and sulfur used in the kraft process (Wallberg *et al.* 2003). The ash content of black liquor has been reported to be as much as 30% (Mansouri and Salvadó 2006). It has been reported that kraft lignins contain 1.5 to 3.0% sulfur, some present as elemental sulfur and some organically bound to the lignin (Gellerstedt and Lindfors 1984). Normally, inorganic chemicals are recovered and re-used in the process and the lignin is burned as a fuel. If the black liquor is not processed through the recovery system, then there will be a large proportion of these chemicals left in the liquor, as evidenced by the high ash (inorganic) content of L2. The elemental composition of L2 ash can be seen in Fig. 2b, showing the presence of K, Na, Al, S, and Si in both the original and purified lignins.

In both L1 and L2, the inorganic content was reduced after the isolation process. The ash content of L2 was reduced from 36.29% to 1.54%, whereas the ash content of the

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original L1 was reduced to 0.45% from 2.31%. For the L2 sample, possible contaminants, such as sodium sulfate and sodium sulfide, would be solubilized in the sodium hydroxide used in the Abacherli and Doppenberg (2001) method and removed from the sample during purification. It can be seen in both the L1 and L2 samples that sulfur was present and may be due to the sulfuric acid used in the purification process. It is important to note that the ash content in the original L1 (steam-exploded process) was much lower than that in the original L2 (kraft process).

L3 is commercial purified kraft lignin made from pine species isolated through an acid hydrolysis process (Beis *et al.* 2010). This commercial lignin had a relatively high ash content (4.25%) as compared to the ash content of the lignins purified by the Abacherli and Doppenberg (2001) method. The percentage ash of the commercial L3 was reported by Cateto *et al.* (2009) as 3%. The ash content may be attributed to the sodium salts and the chemically bonded sulfur from the kraft process. L4 is also a commercial lignin, which is derived from wheat straw through a soda process and acid precipitation technique. The ash content of L4 (soda lignin) was 2.04%, which was lower than the ash content of L3 (kraft lignin). The EDS spectra (Fig. 2c and 2d) showed the presence of K, Na, Al, Si, and S in both commercial samples. The ash and silicate contents of the wheat straw soda lignin were reported by Gosselink *et al.* (2004a) as 1.9% and 0.7%, respectively.
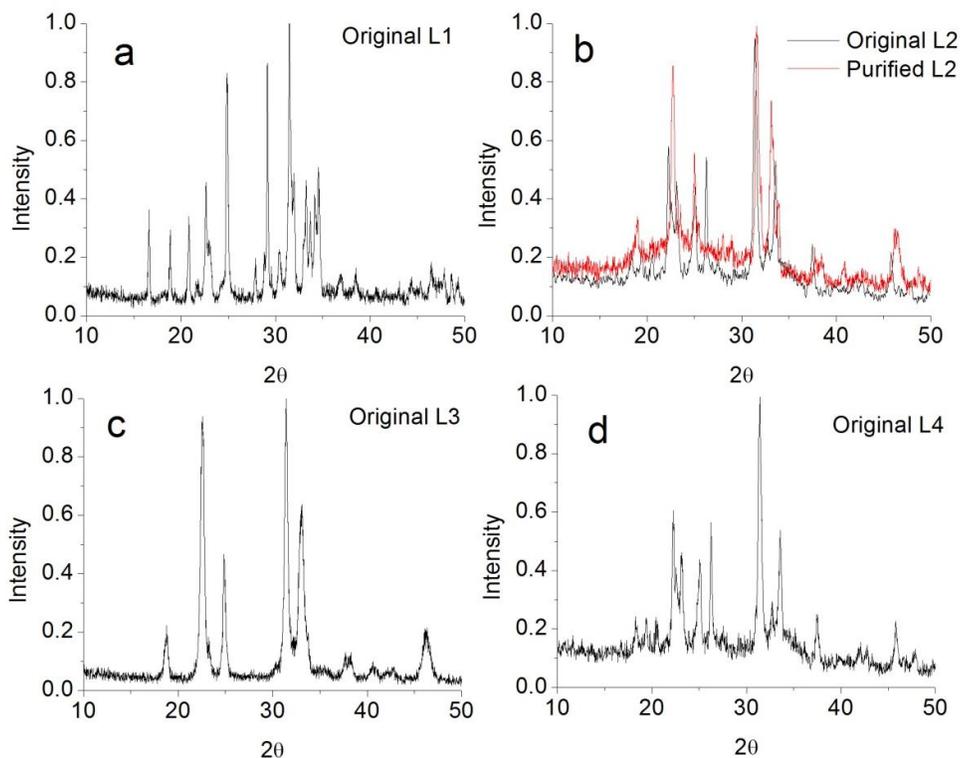


**Fig. 2.** EDS analysis of lignin ash

The moisture content of all isolated lignins was less than 2.5% due to lignin's low affinity to moisture caused by its hydrophobic structure. The original L1 and L2 lignins contained more moisture than their purified forms. Lignin with higher impurities contained more moisture content, which indicated that the impurities contained hydrophilic compounds.

**Table 3.** Ash Content and Moisture Content of Lignin Samples

| Lignin | Ash content | Moisture content |
|---|---|---|
| L1 (original) | 2.31±0.07 | 3.32±0.22 |
| L2 (original) | 36.29±0.29* | 8.05±0.06 |
| L1 (purified) | 0.45±0.09 | 2.50±0.56 |
| L2 (purified) | 1.54±0.13 | 1.13±0.27 |
| L3 (original) | 4.25±0.08 | 1.67±0.32 |
| L4 (original) | 2.04±0.12 | 2.39±1.33 |
| * at 900 °C | | |

Figure 3 shows the X-ray diffraction patterns of lignin ashes. X-ray diffraction scans were run to identify the chemical compounds in each lignin ash. In the XRD scans, the sharp lines matched the spectra of the compounds in the database. In our study, no chemical compound was identified from the XRD pattern of the original L1 (Fig. 3a). Analysis of the original L2 indicated that the ash is a mixture of inorganic compounds. However, the XRD spectrum of the purified L2 ash clearly identified sodium sulfate and silicate in the sample. The XRD spectra showed that the main inorganic compound in L3 lignin was sodium sulfate, while sodium sulfate and silicon dioxide were the two major compounds in L4 specimen (Figs. 3c and 3d).



**Fig. 3.** XRD spectra of lignin ash

## Thermogravimetric Analysis

The thermal characteristics of lignin can be determined using TGA. Figure 4 shows the mass loss of the original and purified lignins over the temperature range of 30

to 1100 °C. The materials were assessed for thermal degradation (on-set temperature), % mass loss between 200 and 600 °C, and percentage of charred residue remaining at 1000 °C (Table 4). The negligible mass loss below 100 °C was a consequence of water loss.

It can be seen in Fig. 4 that the TGA curves of all purified lignins showed very similar thermal behavior. Their thermal degradation began at 200 to 220 °C, which demonstrated that they were thermally stable below 200 °C. Derivative thermograms (dTGs) of purified lignins clearly showed that the thermal activities occurred over the temperature range of 200 to 600 °C. There was an initial rapid degradation until about 350 °C, followed by a much slower rate of degradation, which continued to about 600 °C. L3 exhibited the lowest percentage weight loss (about 54.0%), while the weight loss of other lignins was between 59.0 and 61.0%. The charred residue of purified lignins was in a range of 37 to 45%. The charred residue of L3 (softwood) was the highest, and that of L4 (herbaceous) was the lowest among the lignin samples.

The TGA curves of industrial lignins (original L1 and L2) showed different thermal behaviors. The earlier on-set to thermal degradation for the original L1 could be due to the presence of carbohydrates, which normally show an on-set of degradation below 200 °C.

The larger proportion of mass loss (68.5%) or volatilization of material between 200 and 600 °C can be attributed to the inclusion of carbohydrates in the residue of the original L1. In addition, the lower char of the original L1 (28.1%) in comparison with purified L1 (38.1%) demonstrated that the majority of components were volatilized, thereby indicating that materials such as cellulose and hemicelluloses were present. The original L2 sample demonstrated a different thermal degradation pattern, starting the degradation at a lower temperature (100 °C) than the original L1 (160 °C). The thermogram of the original L2 showed a smaller initial degradation (26.0%) in the 200 to 600 °C range, followed by a gradual degradation from 700 to 900 °C. The second rapid mass loss that occurred was attributed to the degradation of the inorganic impurities, which resulted in a final residue of 24%. In the purified L2 sample, many of the inorganics had already been removed; this can explain the lack of a two-step degradation. The inorganic impurities in the original L2 sample substantially affected the thermal characteristics of this lignin.

Commercial lignins L3 and L4 showed no differences in the thermal degradation of their original and purified forms. Differences in the pyrolysis range of commercial lignins (*e.g.*, L3) have been observed by Beis *et al.* (2010). The results from their TGA analysis showed the same thermal degradation response as was observed in our work. Thus, it appeared that the isolation method removed impurities from the raw lignin, which caused the observed differences in the thermal behavior. The impurities in L1 and L2, which are removed by the purification process, resulted in lignin with the same characteristics as the commercial lignin.

The charred residue of L3 at 1000 °C was about 45%, while for the other samples, it was about 37 to 40%. Above 800 °C, the unvolatilized portion of lignin remains as charred residue due to the formation of highly condensed aromatic structures (Sun *et al.* 2000; Tejado *et al.* 2007). The amount of remaining char was inversely proportional to the amount of hydroxyl, methoxyl, and carboxyl groups (Jakab *et al.* 1995). In other words, higher percentages of charred residue are generated when there are a lower proportion of these functional groups.
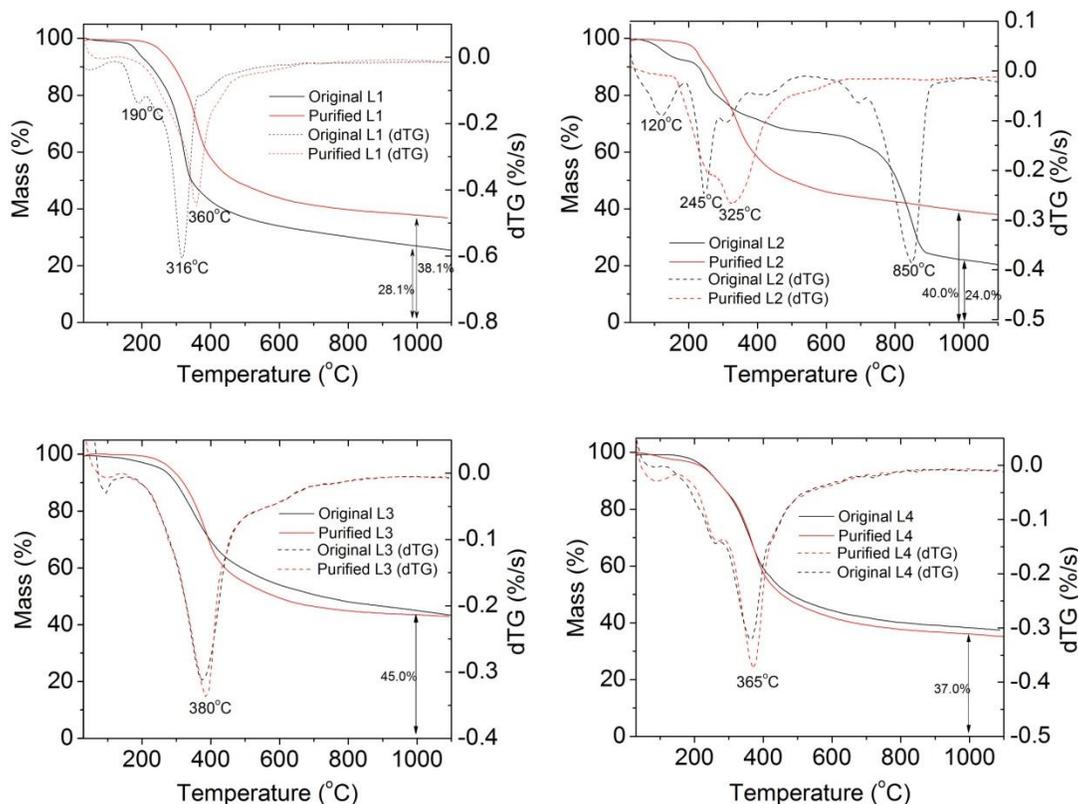
**Fig. 4.** TGA thermogram of original and purified lignin samples

**Table 4.** Onset Temperature, Degradation Temperature, and Percentage of Charred Residues of Original and Purified Lignins

| Lignin | Original | | | Purified | | |
|---|---|---|---|---|---|---|
| | Onset Temp. (°C) | Degradation 200-600 °C (%) | Charred residue (%) | Onset Temp. (°C) | Degradation 200-600 °C (%) | Charred residue (%) |
| L1 | 160.0 | 68.5 | 28.1 | 200.0 | 61.0 | 38.1 |
| L2 | 100.0 | 26.0 | 24.0 | 200.0 | 59.0 | 40.0 |
| L3 | 220.0 | 50.0 | 46.0 | 220.0 | 54.0 | 45.0 |
| L4 | 200.0 | 61.0 | 37.1 | 200.0 | 61.0 | 37.0 |

**Glass Transition**

The DSC results of the original and purified lignins from the third cycle are shown in Fig. 5. The glass transition temperature ($T_g$) and the on-set temperature ($T_0$) of purified lignin were in the range of ~130 to 190 °C and ~120 to 175 °C, respectively. This wide range demonstrated that there were differences between the lignins in terms of flexibility and stiffness at elevated temperatures, which is important in industrial applications. The $T_g$ value can be explained by various molecular factors, such as interchain hydrogen bonding, crosslinking density, rigid phenyl groups, and molecular mass (Heitner *et al.* 2010). Glass transition temperature, molecular weight, and polydispersity correlation for a series of lignin samples was studied by Schmidl (1992). The glass transitions of lignin samples were very broad (ranging from 130 to 170 °C), which reflect the effect of differences in pulping conditions on the molecular weight, and

it was linearly correlated with polydispersity of the molecular weight (Schmidl 1992). On the other hand, the char residue was increased with increasing molecular weight. This effect was explained by Sun *et al.* (2000) in terms of varied in structure and an increasing degree of branching and condensation of lignin structures (Sun *et al.* 2000). Therefore, based on the literature, the glass transition is directly proportional to the char residue. One can see this behaviour with two kraft lignins (L2 and L3), where the char residue and glass transition of L3 was higher than L2, (molecular weight of softwood lignin is greater than hardwood lignin (Tejado *et al.* 2007)). However, this trend may not be consistent for all lignins, because both $T_g$ and char residues also depend on the plant source and extraction conditions.
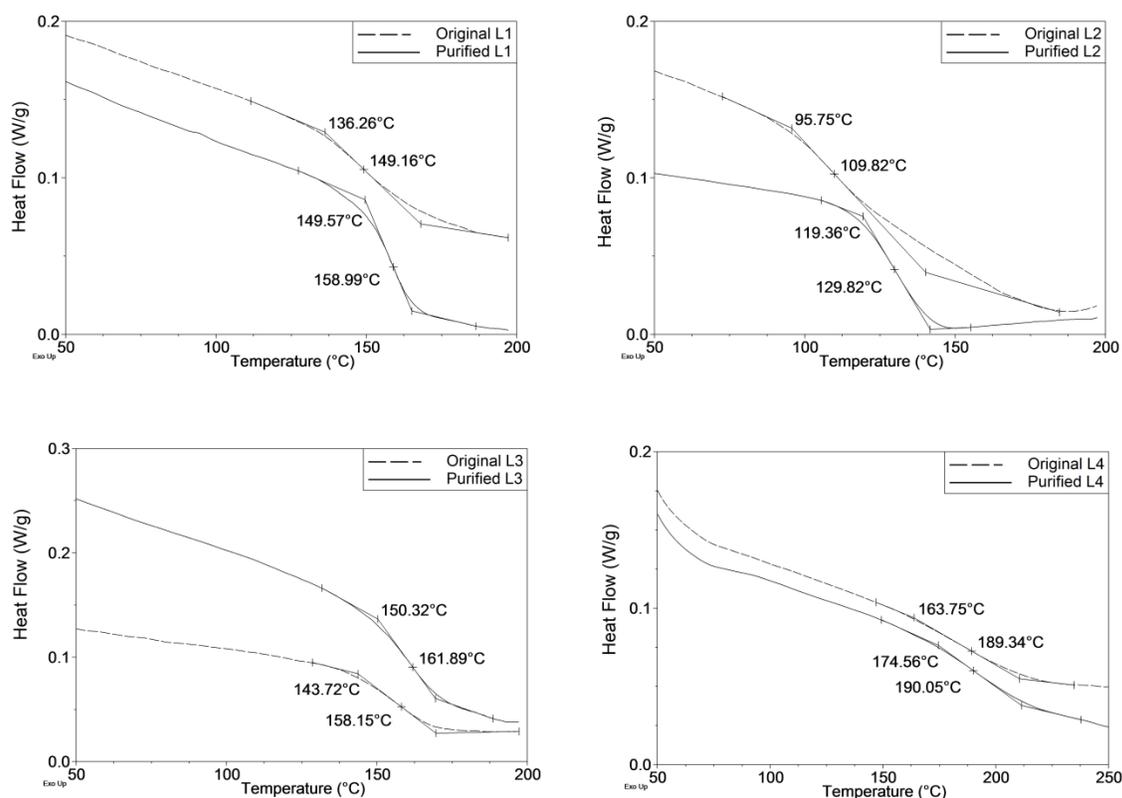


**Fig. 5.** DSC curves of lignin samples

Table 5 shows the $T_g$ and $T_0$ values of the original and purified lignin samples. $T_g$ and $T_0$ were clearly lower in purified lignins than they were in the original lignins. Higher amounts of impurities resulted in larger differences in glass transmission temperatures ($\Delta T_g$) and on-set temperature ($\Delta T_0$). The $T_g$ values for various lignins have been reported in the literature in the range of 90 to 180 °C (Glasser and Jain 1993; Tejado *et al.* 2007), with higher values corresponding to softwood lignins. The $T_g$ and $T_0$ of purified L1 were very similar to those of the original L3. It seems that the L1 and L3 lignins behaved quite similarly once the carbohydrate contaminants were removed through the purification process. The low $T_g$ of the original L2 suggested that there may be other polyphenoic macromolecules, in addition to lignin, present in the sample (Sahoo *et al.* 2011). The purified L2 remained quite different from the other samples, with lower $T_g$ and $T_0$.

**Table 5.** Onset Temperature and Glass Transition Temperature for Original and Isolated Lignin Samples

| Lignin | On-set Temp. ($T_0$) (°C) | | | Glass Transition Temp. ($T_g$) (°C) | | |
|---|---|---|---|---|---|---|
| | Original | Purified | $\Delta T_0$ | Original | Purified | $\Delta T_g$ |
| L1 | 136.26 | 149.57 | 13.31 | 149.16 | 158.99 | 9.83 |
| L2 | 95.75 | 119.36 | 23.61 | 109.82 | 129.82 | 20.00 |
| L3 | 143.72 | 150.32 | 6.60 | 158.15 | 161.89 | 3.74 |
| L4 | 163.75 | 174.56 | 10.81 | 189.34 | 190.05 | 0.62 |

## CONCLUSIONS

1. The main differences between industrial and commercial lignins can be found in their impurities. The impurities in industrial lignins depended on the extraction process and the source of the lignocellulosic material. The inorganic elements in industrial lignin were reduced after the isolation process. Industrial processes such as kraft generate more impurities when compared to steam explosion. Extracted lignin from wheat straw contained more silicon than hardwood and softwood lignins.

2. The thermal decomposition and percentage of the charred residue of isolated lignins were slightly different from each other. However, the percentage of charred residue in industrial lignins was much higher than that in isolated lignins.

3. The glass transition temperature of lignin samples is reduced with higher percentages of impurities. There was a wide range of $T_g$ (~130 to 190 °C) for isolated lignins.

4. Industrial lignins, which have lower costs, can be beneficially utilized once their important characteristics are known. This elemental and thermal analysis of two industrial lignins suggested that steam-exploded lignin may have higher potential for economic return, for instance in carbon fiber production, in comparison with kraft lignin due to its lower inorganic content.

## ACKNOWLEDGMENTS

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