

## CHEMICAL AND THERMAL CHARACTERIZATION OF THREE INDUSTRIAL LIGNINS AND THEIR CORRESPONDING LIGNIN ESTERS

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Corn stover and rice straw lignin samples received from ethanol pilot plants, along with softwood kraft lignin samples, were characterized using pyrolysis GC-MS, <sup>13</sup>C CP/MAS NMR spectroscopy, and permanganate oxidation degradation. The lignins were then esterified using 1-methylimidazole as a catalyst in a pyridine-free reaction, and the thermal properties of the products were evaluated. Solid state NMR showed the rice straw lignin contained 18% residual polysaccharides. Pyrolysis GC-MS showed the softwood kraft, corn stover, and rice straw lignins to be G – type, H/G/S – type, and G/S – type, respectively. However, some discrepancy was apparent between the pyrolysis and permanganate oxidation studies as to the ratios of the monomeric make-up of the lignins. The kraft and rice straw lignins were determined to have high degrees of condensation, while the corn stover lignin was uncondensed. Little to no increase in solubility was noticed for corn stover or rice straw lignin esters in organic solvents. Glass transition temperatures ( $T_g$ ) of the lignin derivatives were determined by a combination of differential scanning calorimetry, dynamic mechanical analysis, and parallel plate rheometry.

*Keywords:* Bioplastic; Esterification; Lignin; Thermal analysis

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### INTRODUCTION

Lignin is a propylphenol-based natural polymer that is one of the major structural chemical components of all woody plants. Along with the other two major components, cellulose and hemicellulose, lignin helps form a composite system capable of imparting the strength and rigidity necessary for tall plant growth. However, lignin presents a problem to industries intent on obtaining the polysaccharide fibers in plants, such as in paper production or for feedstocks for cellulosic ethanol. The polysaccharides must be separated from the rest of the plant, usually by chemical or enzymatic means, leaving behind a lignin-rich material of little value. Indeed, huge amounts of lignin are isolated by industry annually, and the bulk of it is either burned to recover energy or is otherwise considered waste. Only about 1 to 2% of this lignin is used to make other products (Lora and Glasser 2002).

Considerable effort had been made to try and utilize this large surplus of industrial lignin. In particular, researchers have wanted to take advantage of lignin's renewable nature and use it as a feedstock to make products that could substitute for

petroleum-derived materials. Despite some promising avenues of research into lignin utilization, only limited success has been realized so far in moving lignin utilization up from a laboratory scale to an industrial scale. This is largely due to the highly variable nature of lignin, as its chemistry changes depending on its plant source and the method by which it was isolated. It still thought, though, that by developing a better understanding of the lignin molecule and by continuing research into its utilization, lignin's potential as a renewable and widely available raw material can be unlocked (Lindberg et al. 1989; Feldman 2002).

The research presented here investigates two previously uncharacterized lignins that are byproducts of pilot plants for producing cellulosic ethanol. One of the lignins is the result of enzymatic hydrolysis of corn stover, while the second comes from a 2-stage acid hydrolysis of rice straw. These two lignins were chemically characterized and then esterified to evaluate their resulting thermoplastic properties. A third frequently studied lignin, softwood kraft lignin, was also investigated here and used to validate the methods.

## EXPERIMENTAL

### Materials

Indulin AT (softwood kraft lignin) was obtained from MeadWestvaco. Corn stover lignin, generated after enzymatic hydrolysis, was obtained from the National Renewable Energy Laboratory (Golden, CO). Rice straw lignin, generated after a two-stage sulfuric acid hydrolysis, was obtained from Arkenol, Inc (Irvine, CA). Both the corn stover and rice straw lignins were extracted with hot water prior to use.

### Methods

#### *Lignin content analysis*

The lignin content of samples from each of the lignin sources was determined using an acid insoluble (Klason) lignin and the acid soluble lignin procedures according to ASTM D1106 and ASTM E1721 methods, respectively (Dence and Lin 1992).

#### *Pyrolysis GC-MS*

Pyrolysis degradation products of each lignin type were analyzed using gas chromatography-mass spectrometry (GC-MS) as a measure of monolignol composition. Lignin samples were pyrolyzed at 450°C using a SGE pyrojector II. The compounds were separated on a 15 m ZB-1 (Phenomenex) capillary column with a temperature profile of 45°C (4 min) followed by a 5°C/min ramp to 290°C (5 min). The pyrolysis products were analyzed by GC-MS (PolarisQ, ThermoQuest), and their identity confirmed by retention time, NIST mass spectral libraries, and by comparison with previously published data (Meier and Faix 1992).

#### *<sup>13</sup>C CP-MAS NMR spectroscopy*

Solid state cross polarization-magic angle spinning (CP-MAS) <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance DRX-400s NMR spectrometer operating at a frequency of 100.6 MHz equipped with a

Chemimagnetics solids probe. Lignin samples were ground prior to being packed into a 5 mm zirconia rotor, and then spun at 5,000 Hz. A 3.75  $\mu$ s proton preparation pulse was followed by a 1 ms cross polarization contact time. The acquisition time was 6.6  $\mu$ s, and the spectra were the result of 512 scans.

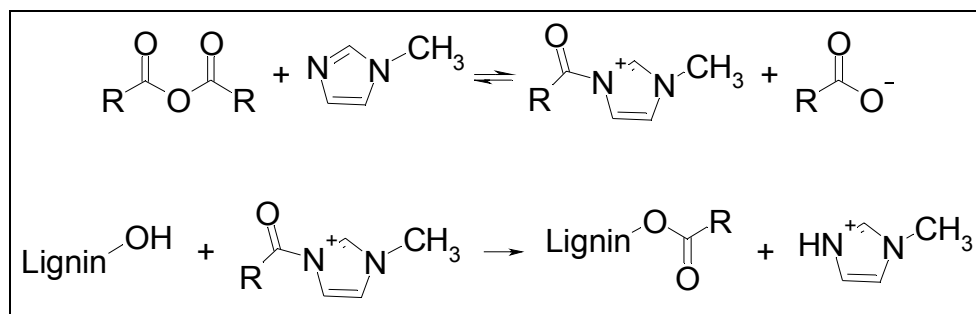
#### *Permanganate oxidation*

Lignin samples were subjected to oxidative degradation to evaluate their monolignol composition and inter-monomeric linkages (Gellerstedt 1992). This procedure involves four steps: 1) methylation of the lignin samples, 2) oxidative degradation by potassium permanganate and sodium periodate, 3) oxidative degradation by hydrogen peroxide, and 4) methylation of the reaction products for analysis. The final step 4 was modified from the original procedure due to safety concerns and N,N-dimethylformamide dimethyl acetal (Methyl-8 Reagent, Pierce) was used as the methylating reagent. An internal standard for GC-MS analysis was created by reacting pyromellitic acid with Methyl-8 Reagent. Pyromellitic acid tetramethyl ester was dissolved in dichloromethane, and the precise concentration of the solution was determined by GC-MS analysis with a known amount of methyl benzoate. The lignin oxidative degradation products were methylated after being dissolved in 1.0 mL dichloromethane by the addition of 0.5 mL of Methyl-8 Reagent. After reacting for 10 min, 1.0 mL of the internal standard solution was added, and the mixture was analyzed by GC-MS. Separations by GC-MS (PolarisQ, ThermoQuest) were achieved with a 30 m ZB-1 (Phenomenex) capillary column using a temperature profile of 40 °C (1 min), followed by a 40°C/min ramp to 120°C, followed by a 5°C/min ramp to 270°C (20 min). The identities of the compounds were confirmed by retention time, NIST mass spectral libraries, and by comparison with previously published data (Chen 1988).

Quantification of the resulting aromatic carboxylic acid methyl esters was accomplished by integrating their peak areas and comparing them to the internal standard peak area. The yields of degradation products with one carboxymethyl group per molecule were divided by 0.6, while those with two carboxymethyl groups per molecule were divided by 0.36 (Gellerstedt 1992). This procedure compensates for incomplete oxidation of lignin and provides for more accurate theoretical yields of the degradation products.

#### *Lignin esterification*

Samples of each lignin type were measured in 10 g portions into a 250 mL round-bottomed flask and equilibrated to 65°C. Either acetic, propionic, or butyric acid anhydride was added to the flask. In the case of kraft lignin, 50 mL of the acid anhydride was used, while 75 mL of acid anhydride was added to the corn stover and rice straw lignins. To each reaction mixture, 1 mL of 1-methylimidazole was added as a catalyst and the reaction was stirred for 24 hours under reflux. To quench the reaction, water was added and the mixture stirred in chilled water bath. Once the flask had cooled, the precipitated lignin was removed by filtration. The collected lignin was thoroughly washed with water to remove any residual carboxylic acid and catalyst. The esterified lignin was dried under reduced pressure and weighed to record a yield. Figure 1 shows the reaction mechanism for esterifying lignin with 1-methylimidazole as a catalyst.



**Fig. 1.** Reaction mechanism for lignin esterification using 1-methylimidazole as a catalyst (Connors and Pandit 1978). R =  $-\text{CH}_3$  for acetic anhydride,  $-\text{CH}_2\text{CH}_3$  for propionic anhydride, and  $-\text{CH}_2\text{CH}_2\text{CH}_3$  for butyric anhydride.

Infrared spectra of the lignins and lignin esters were obtained on a ThermoNicolet Avatar 370 spectrometer using a diffuse reflectance module (128 scans). Dry lignin samples were weighed (20 mg) and then ground into 0.5 g of FTIR grade potassium bromide with a mortar and pestle. The samples were vacuum dried prior to analysis.

#### *Differential scanning calorimetry*

Differential scanning calorimetry (DSC) was performed on 10-15 mg of lignin in sealed aluminum pans. Prior to running DSC scans, samples were allowed to anneal overnight at temperatures a few degrees below their glass transition temperature ( $T_g$ ). Scans were run from 30 to 250°C at a 5 °C/min ramp under nitrogen using a TA 2910 DSC instrument. Data were analyzed using TA Instruments Universal Analysis Software.

#### *Dynamic mechanical analysis*

Dynamic mechanical analysis (DMA) samples were formed by compression molding in a matched barrel and plunger using a 30 ton hydraulic hot press (PHI). About 2 g of modified lignin was pressed at 150°C and 8.96 MPa into disks approximately 25 mm in diameter and 2 mm thick. A 10 mm wide strip was then cut from the middle. The dimensions of this strip were measured accurately with calipers and loaded onto a TA Q800 DMA instrument with 20 mm span 3-point bending clamps. Stress-strain curves were obtained at 30°C using a 0.5 N/min ramp force according to ASTM D 5934. Temperature sweeps were performed from 30 to 250°C at 3°C/min using a strain of 0.03% and a frequency of 1 Hz. Two duplicate specimens were run for every modified lignin sample. Data was analyzed using TA Instruments Universal Analysis software.

#### *Rheology*

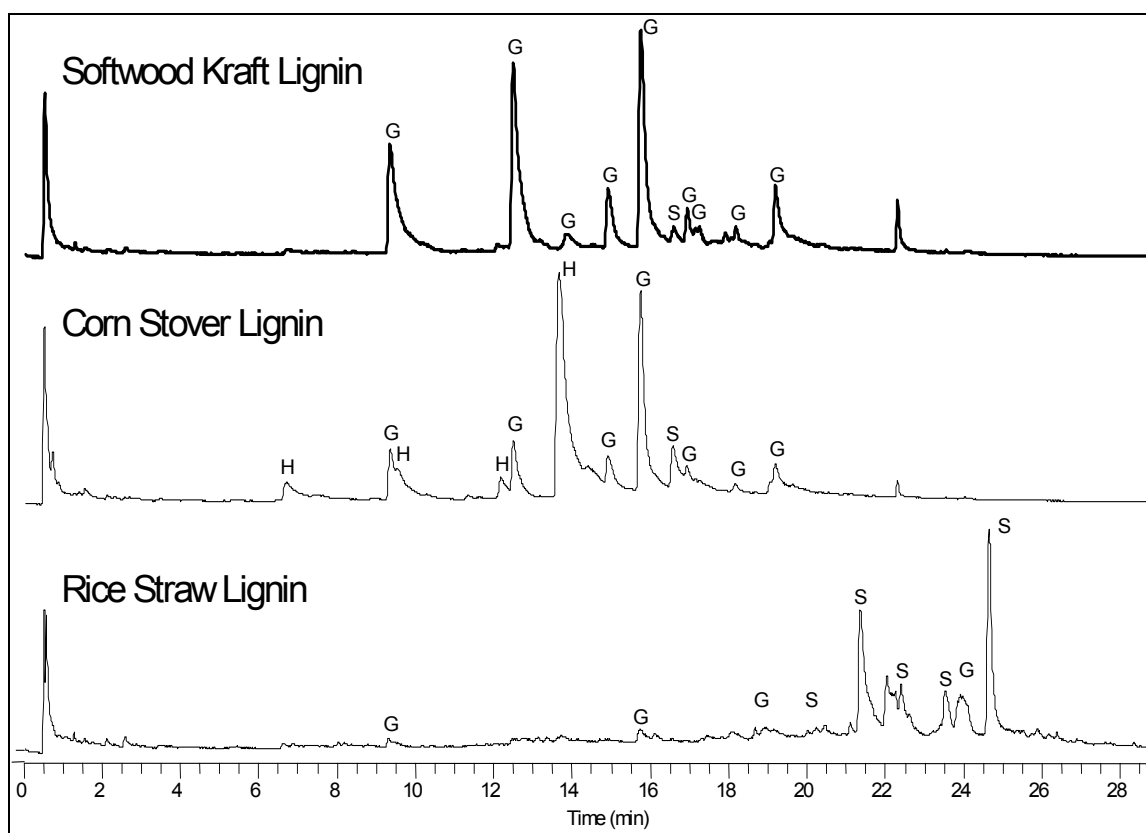
Parallel plate rheometry was performed using a Bohlin CVO100 instrument equipped with an extended temperature unit. Samples were compression molded as described above into 25 mm disks. Temperature sweeps were performed from 150 to 50°C at 2°C/min decreasing ramp. The oscillation frequency was kept constant at 1Hz, the normal force at 1 N, and a strain of 0.05%. Data was analyzed using the Bohlin rheology software v06.32.

## RESULTS AND DISCUSSION

### Lignin Content and Composition of the Different Samples

Klason lignin and acid soluble analyses showed that the kraft, corn stover, and rice straw lignin samples contained 95, 85, and 82% total lignin, respectively.

Pyrolysis GC-MS provides a rapid procedure for analyzing the monolignol composition of lignin samples (Fig. 2). Pyrolysis products were derived from *p*-hydroxyphenyl (H), guaiacyl (G), or syringyl (S) propane units. As expected, kraft lignin is shown to consist mostly of guaiacyl-based monomers. Corn stover lignin consists of a ratio of *p*-hydroxyphenyl to guaiacyl to syringyl-based units (*H/G/S* ratio) of approximately 0.90/1.00/0.07. Therefore this lignin could be considered a *p*-hydroxyphenyl-guaiacyl lignin. The rice straw lignin contained little *p*-hydroxyphenyl lignin, and close to 1 guaiacyl lignin unit for every 3 syringyl lignin units. Therefore it can be considered a guaiacyl-syringyl type lignin.

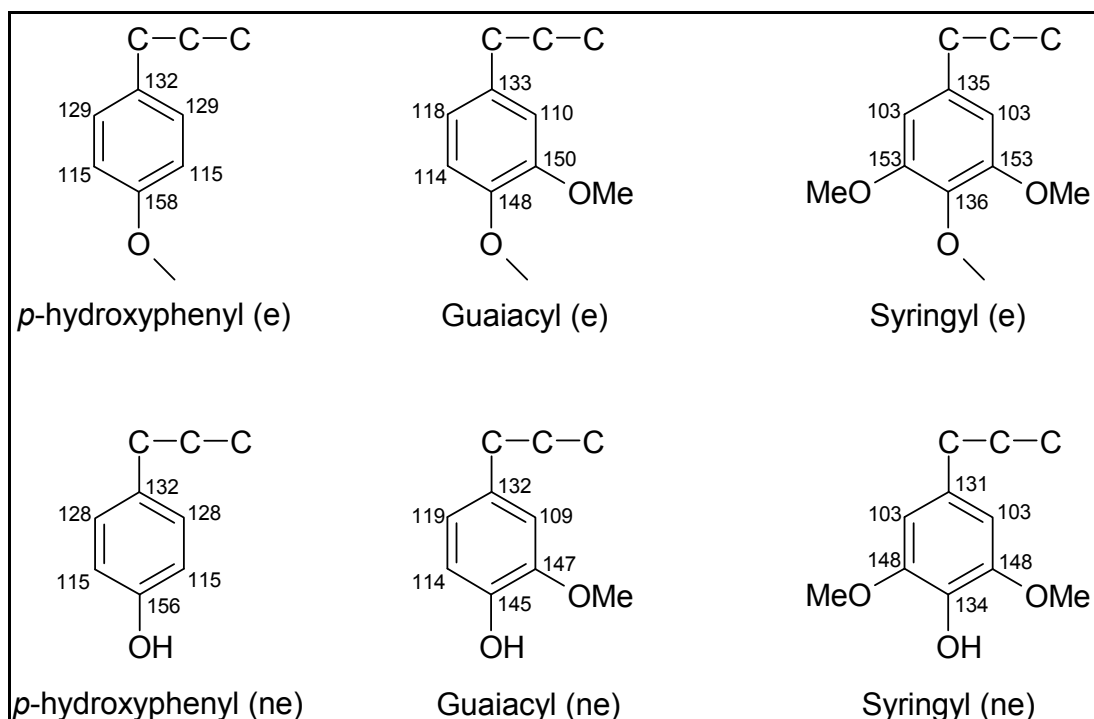


**Fig. 2.** Pyrolysis GC-MS total ion current chromatograms of the lignins studied. Peaks labeled with *H* represent compounds derived from *p*-hydroxyphenyl units, peaks labeled with *G* represent compounds derived from guaiacyl units, and peaks labeled with *S* represent compounds derived from syringyl units.

### <sup>13</sup>C CP/MAS NMR Analysis

Chemical shift assignments for solid state <sup>13</sup>C spectra of lignin were partially interpreted due to the fact that lignin is a very heterogeneous polymer, and many signals can overlap (Leary and Newman 1992). Aromatic carbon signals occur in the range of 100 to 155 ppm, while signals from aliphatic carbons occur between 20 and 90 ppm. The most prominent signal in the lignin <sup>13</sup>C spectra occurs at 55 to 56 ppm, attributed to methoxy carbons on guaiacyl and syringyl units. Other major signals occur between 145 and 155 ppm. These signals are due to the carbons 3 and 4 on guaiacyl phenolic units and carbons 3 and 5 on syringyl units. Common aromatic carbon chemical shifts from lignin model compounds are shown in Fig. 3.

Despite the difficulty of deriving detailed chemical information from lignin using solid-state <sup>13</sup>C NMR, the spectra were useful in this study for identifying residual carbohydrate in the corn stover and rice straw lignin samples. This was evident in the sharp doublet centered at 73 ppm (carbons 2, 3, and 5 on a glycopyranosyl ring), the strong signal at 105 ppm (carbon 1 on a β-glucopyranoside unit of cellulose), and two peaks at 85 and 89 ppm (carbon 4 of amorphous and crystalline cellulose, respectively) (Gauthier et al. 2003). The presence of carbohydrates in the rice straw lignin is much greater than in the corn stover lignin. The softwood kraft lignin spectra showed little evidence of carbohydrate in the sample (Fig. 4). This is consistent with the Klason lignin analysis of these lignin samples which indicated a relative purity of rice straw lignin < corn stover lignin < softwood kraft lignin.



**Fig. 3.** <sup>13</sup>C NMR shifts (ppm) for aromatic carbon atoms in lignin model compounds. (e) = etherified. (ne) = non-etherified (Sipilä and Syrjänen 1995)

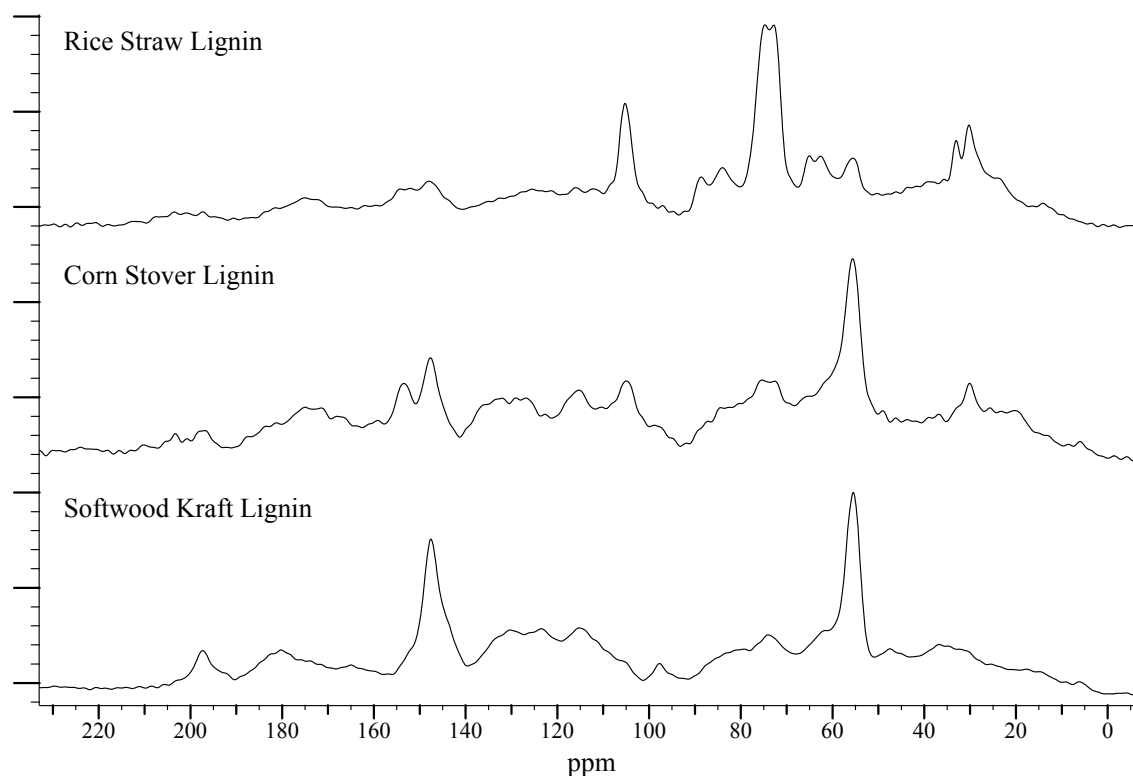


Fig. 4.  $^{13}\text{C}$  CP/MAS NMR spectra obtained for softwood kraft, corn stover, and rice straw lignins

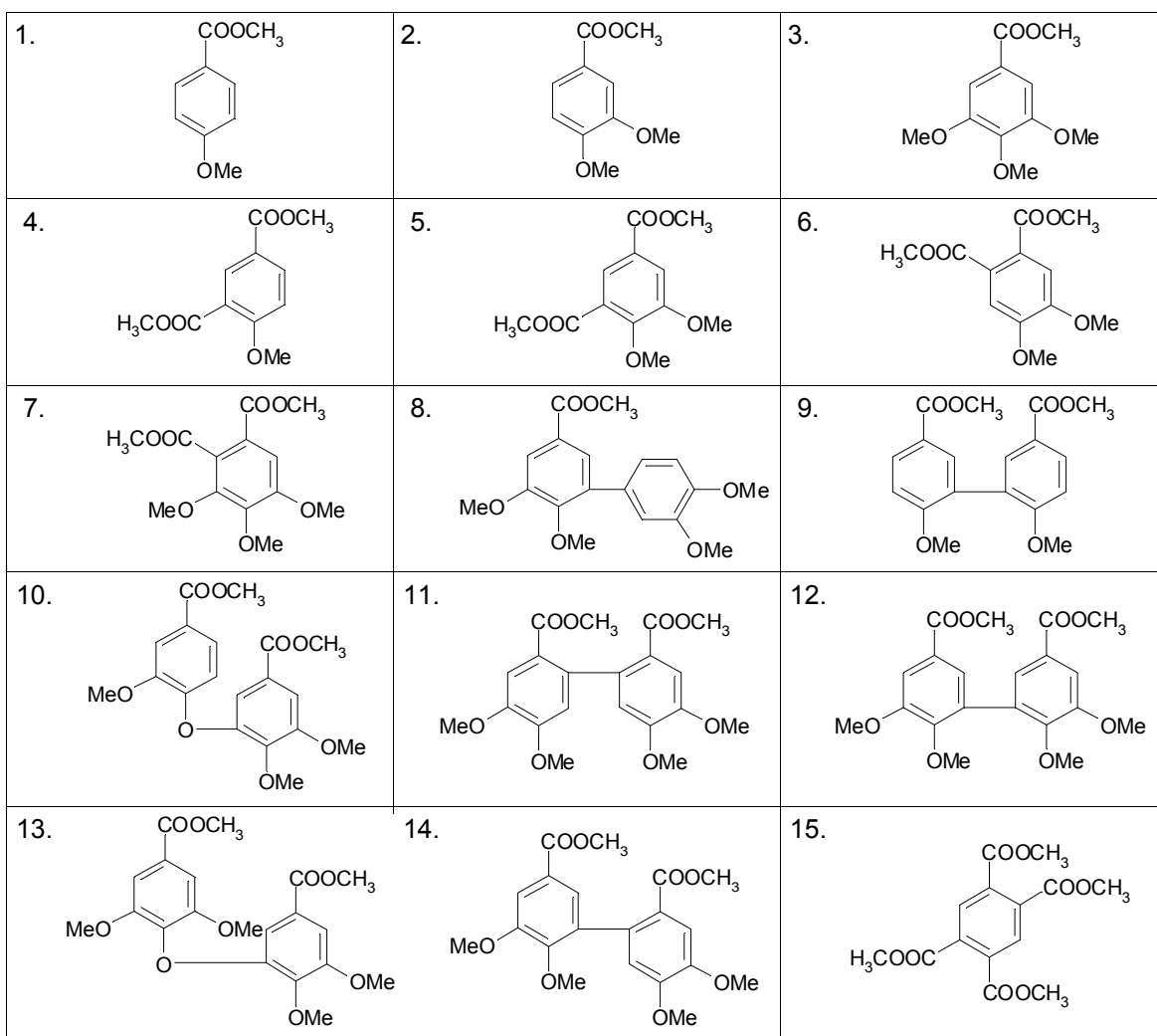
### Monolignol Composition and Linkage Analysis by Permanganate Oxidation

Chemical degradation of lignin by permanganate oxidation was used to obtain monomeric composition and intermonomeric linkage information in lignin. Only lignin units carrying free phenolic groups was analyzed, and therefore the analysis shows data from a fraction of lignin. However, assumptions were made that are recognized to give an accurate representation of the entire lignin structure (Gellerstedt 1992). Permanganate oxidation of lignin is a four step method that degrades aliphatic (propyl) chains in the lignin molecule, which results is a mixture of aromatic carboxylic acids and analyzed as their methyl esters by GC-MS (Fig. 5). Compound 15 is the internal standard.

An example chromatogram obtained from analysis of lignin permanganate oxidation degradation products is shown in Fig. 6. Each degradation compound identified by GC-MS can be characterized as derived from *p*-hydroxyphenyl (H), guaiacyl (G), or syringyl (S) propane units. Quantification of these compounds was employed to also determine monomeric composition of a lignin sample. Each compound also yields information about inter-monolignol linkages within the lignin sample. Compounds 1, 2, and 3 come from uncondensed phenolic end groups. Compounds (4, 5, 6, and 7) that contain two carboxy-methyl groups on an aromatic ring are derived from phenolic end groups that had a carbon-carbon linkage from its 5 or 6 position on the ring to an adjacent lignin unit. The degradation compounds containing two aromatic rings represent structures with the lignin sample that contained diaryl (8, 9, 11, 12, and 14) or diaryl ether (10 and 13) linkages (Gellerstedt 1992). From the data provided, a condensation factor can be calculated for the lignin sample. This is defined as the molar ratio of

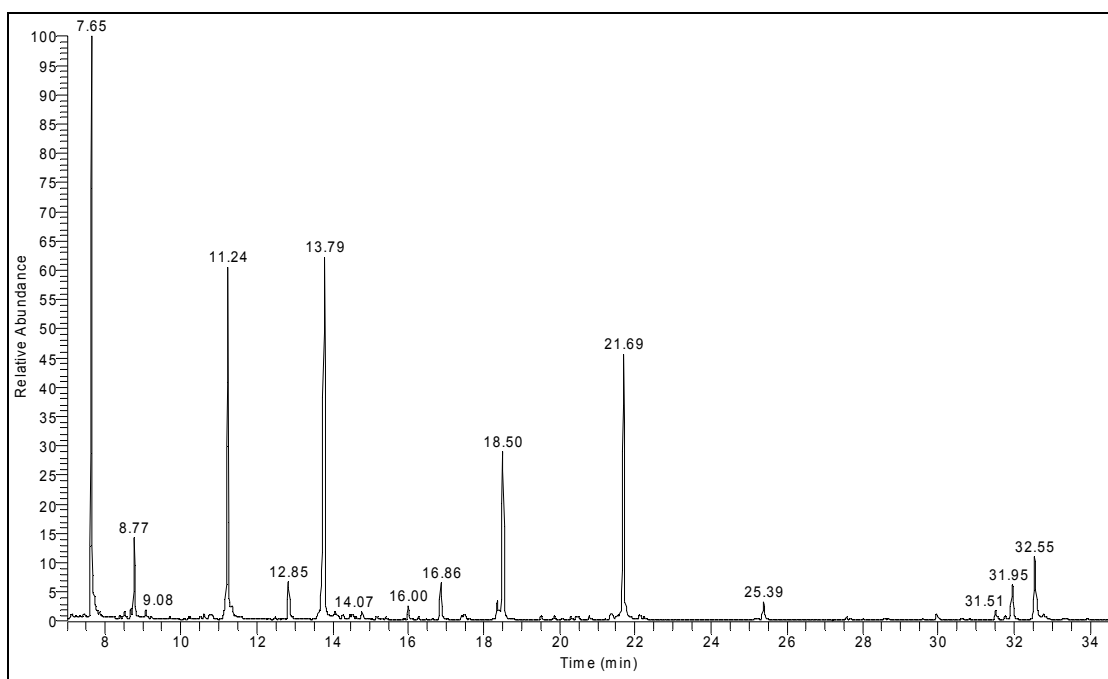
monobasic to dibasic monomers (the sum of compounds 1 through 3 to the sum of compounds 4 through 7) (Glasser 2000). The condensation factor gives a quantifiable value to use when comparing the degree of condensation between different lignin samples. Lignin with low condensation factors contain many carbon-carbon bonds with relatively few alkyl aryl ether bonds, and therefore are highly condensed. Lignin with high condensation factors contain a large percentage of alkyl aryl ether bonds and are relatively uncondensed. High condensation factors generally indicate a lignin sample that closely represents lignin in its native state.

Previous experiments have shown that the yields of compounds given by GC-MS need to be corrected due to incomplete oxidation (Gellerstedt 1992). The yields of uncondensed structures (compounds 1 through 3) need to be divided by 0.6, while the yields of condensed structures (compounds 4 through 14) need to be divided by 0.36 (Table 1). Table 1 shows a tabulation of the adjusted yields obtained by this study.



**Fig. 5.** Permanganate oxidation degradation products identified by GC-MS





**Fig. 6.** GC-MS total ion chromatogram of permanganate oxidation degradation products from corn stover lignin

**Table 1.** Yields of Permanganate Oxidation Products from Softwood Kraft, Corn Stover, and Rice Straw Lignins

Compound	Retention Time (min.)	Adjusted Yields (mol %)		
		Softwood Kraft Lignin	Corn Stover Lignin	Rice Straw Lignin
1	7.6	7.1	38.7	21.0
2	11.2	47.8	20.7	28.2
3	13.8	5.3	24.2	14.5
4	14.8	0.8	0.7	3.4
5	16.9	17.5	3.5	8.3
6	17.5	4.5	2.0	4.7
7	19.5	0.2	0.3	1.1
8	26.0	0.9	0.0	0.7
9	30.0	0.1	0.7	2.4
10	31.5	3.1	0.9	2.2
11	31.8	0.0	0.3	0.0
12	32.0	12.2	2.7	6.5
13	32.6	0.4	4.9	7.0
14	32.8	0.0	0.4	0.0

The yields of permanganate oxidation products from softwood kraft lignin (condensation factor of 2.6) are consistent with those observed by other researchers, (condensation factor of 2.1) indicating a relatively condensed structure consisting of mainly G based monomeric units (Glasser et al. 1983; Gellerstedt and Lindfors 1984). The *H/G/S* ratio of softwood kraft lignin according to this method is 0.09/1.0/0.08, which is a similar result to that obtained by pyrolysis GC-MS analysis. The condensed structures in kraft lignin are represented by aliphatic-5 and 5-5 carbon linkages and deduced from the abundance of compounds 5 and 12.

The corn stover lignin has a relatively uncondensed structure and an *H/G/S* ratio of 1.3/1.0/0.94 according to this analysis. The high condensation factor of 12.9 of the corn stover lignin sample indicates that its chemistry is not highly altered from its native structure by enzymatic treatment. There is an apparent discrepancy between the monomeric composition determined by permanganate oxidation and pyrolysis GC-MS. It has been reported that when one uses the pyrolysis GC-MS method to determine *H/G/S* ratios, the syringyl groups are generally under-represented (Faix et al. 1994). Work by Nonier et al. (2006) has shown that the G/S ratio was positively correlated to pyrolysis temperature and that at the pyrolysis temperatures employed in this study (450°C) low *S* values would be expected.

The rice straw lignin had a condensation factor of 3.6, indicating a fairly condensed lignin structure. Condensed structures are represented by alkyl aryl carbon-carbon linkages at the 2, 5, and 6 positions on the aromatic rings. Other prevalent condensed structures include 5-5 diaryl linkages and 4-*O*-5 diaryl ether linkages. A previous study on acid hydrolysis wood lignin reports condensation factors between 0.3 and 0.8 (Glasser et al. 1983). The high condensation factor of rice straw lignin compared to these values may indicate a lower level of hydrolysis. This may also be a reason for the high residual carbohydrate content in this lignin. In addition, previous work has indicated that acid hydrolysis lignin may contain a large number of  $\alpha$ -5 and  $\alpha$ -6 linkages (Yasuda and Terashima 1982). Degradation products from these types of condensed structures may be underrepresented in the analysis due to the formation of diaryl ketone structures (Meguro et al. 1998). The *H/G/S* ratio of 0.72/1.0/0.46 for rice straw lignin determined by permanganate oxidation is not in close agreement with that determined by pyrolysis GC-MS (0.09/1.0/0.08) as described above. However, the ratio determined by permanganate oxidation is in much better agreement with a previous study that examined rice straw lignin using quantitative <sup>13</sup>C NMR techniques, which calculated an *H/G/S* ratio of 0.82/1.0/0.45 (Lora 2002).

Allowing the initial methylation step to proceed for 36 hours and at a pH of 13 may increase the yield of condensed structures from permanganate oxidation and give a more accurate representative value for lignin condensation (Gellerstedt 1992; Marques et al. 1999).

### **Esterification of Softwood Kraft, Corn Stover, and Rice Lignins**

Yields (weight % gain) of acetic, propionic, and butyric lignin esters obtained for softwood kraft, corn stover, and rice straw lignins are given in Table 2. A previous study (Steward et al. 2002) obtained similar yields of softwood kraft acetate and butyrate lignin esters. Based on molar weights of acetate, propionate, and butyrate substituents

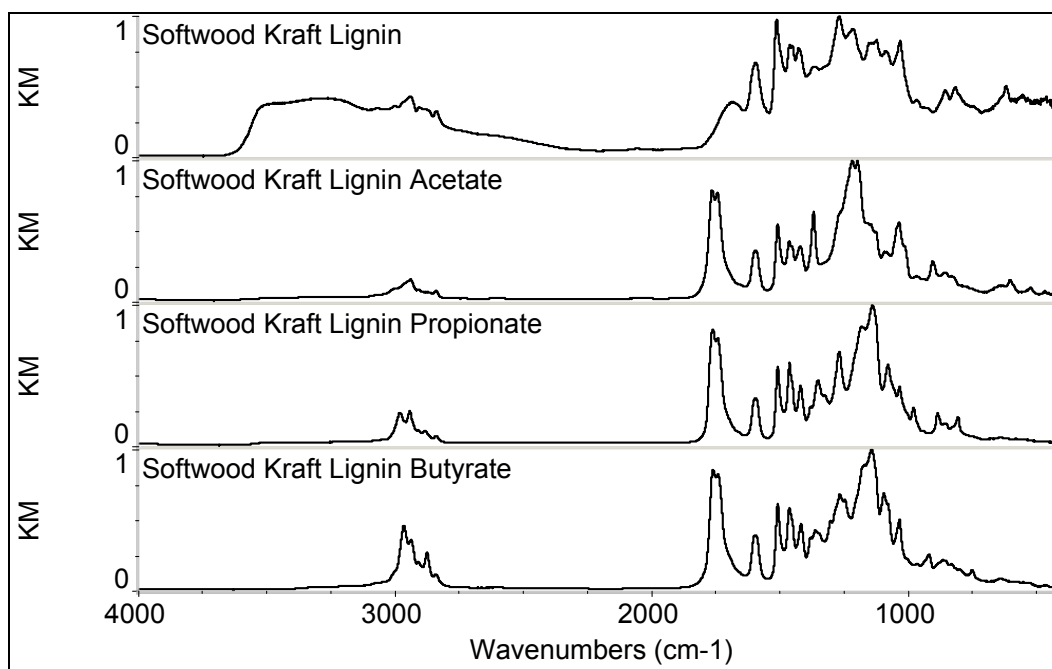
(43, 57, and 71 g/mol, respectively), there is an apparent increase in the degree of substitution in lignin esters as the size of the substituent increases.

**Table 2.** Yields (weight % gains) of Softwood Kraft, Corn Stover, and Rice Straw Lignin upon Esterification

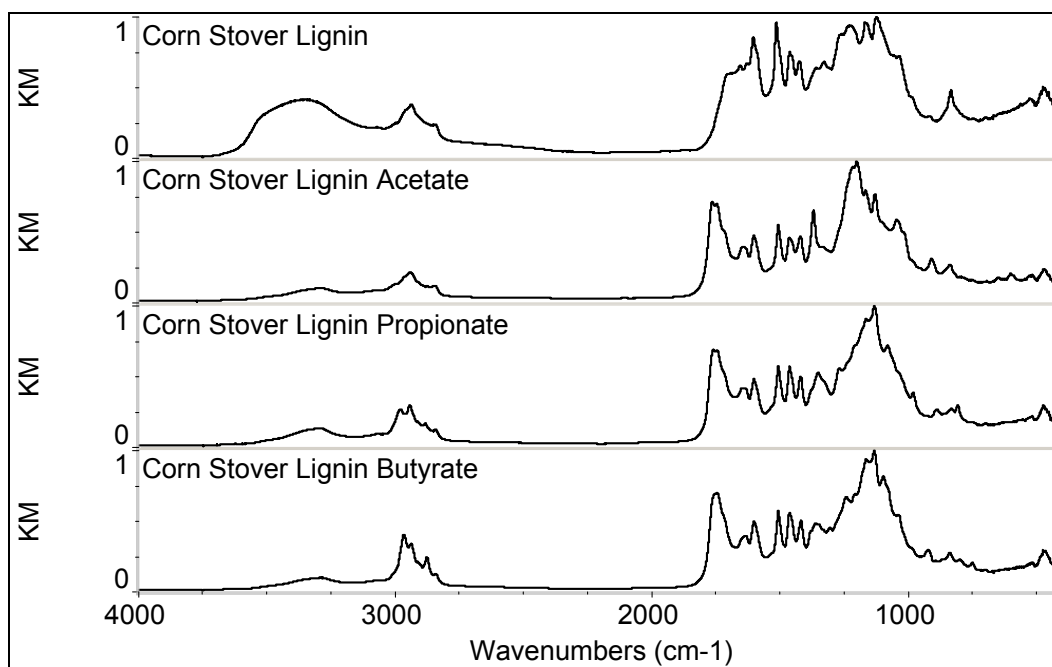
Ester	Softwood Kraft	Corn Stover		Rice Straw
		(weight % gain)		
Acetate	20	18	17	
Propionate	29	24	15	
Butyrate	53	30	23	

Infrared spectra of the modified lignin samples were compared to spectra of original lignin samples to establish the extent of esterification reactions (Figs. 7-9). Esterification reactions resulted in the drastic reduction of the OH absorption band at 3400-3500  $\text{cm}^{-1}$ , along with the appearance of a major absorption band at 1740-1770  $\text{cm}^{-1}$  (C=O stretch). Other absorption bands appeared at 1350-1380  $\text{cm}^{-1}$  (aliphatic C-C stretch), as well as a cluster of bands with maxima between 1200 and 1250  $\text{cm}^{-1}$  (C-C, C-O, and C=O stretches). The intensity of aliphatic C-H stretches (2850-2950  $\text{cm}^{-1}$ ) increased as the alkanoate chain length increased (Figs. 7 to 9). These results were comparable to previously published data on lignin esterification in the presence of pyridine (Faix 1992; Glasser 1993). The spectra for all the modified kraft lignin samples indicate that the esterification reactions essentially went to completion, with the exceptions of esterified rice straw and, to a lesser extent, corn stover lignins. The rice straw lignin ester IR spectra show an OH absorption, possibly due to unreacted hydroxyl groups present in residual plant polysaccharides. The original lignin preparation showed  $^{13}\text{C}$  CP/MAS NMR spectroscopic signals assigned to cellulose, as discussed earlier. In addition, when normalized to the absorption band around 1500  $\text{cm}^{-1}$  (aromatic skeletal vibration), the intensity of the C=O absorption band at  $\approx 1740 \text{ cm}^{-1}$  (1.83) is significantly less than the corresponding absorption bands for rice straw lignin acetate and propionate (2.61 and 2.88, respectively). An incomplete reaction may be why the yield of rice straw lignin butyration reaction was lower than expected.

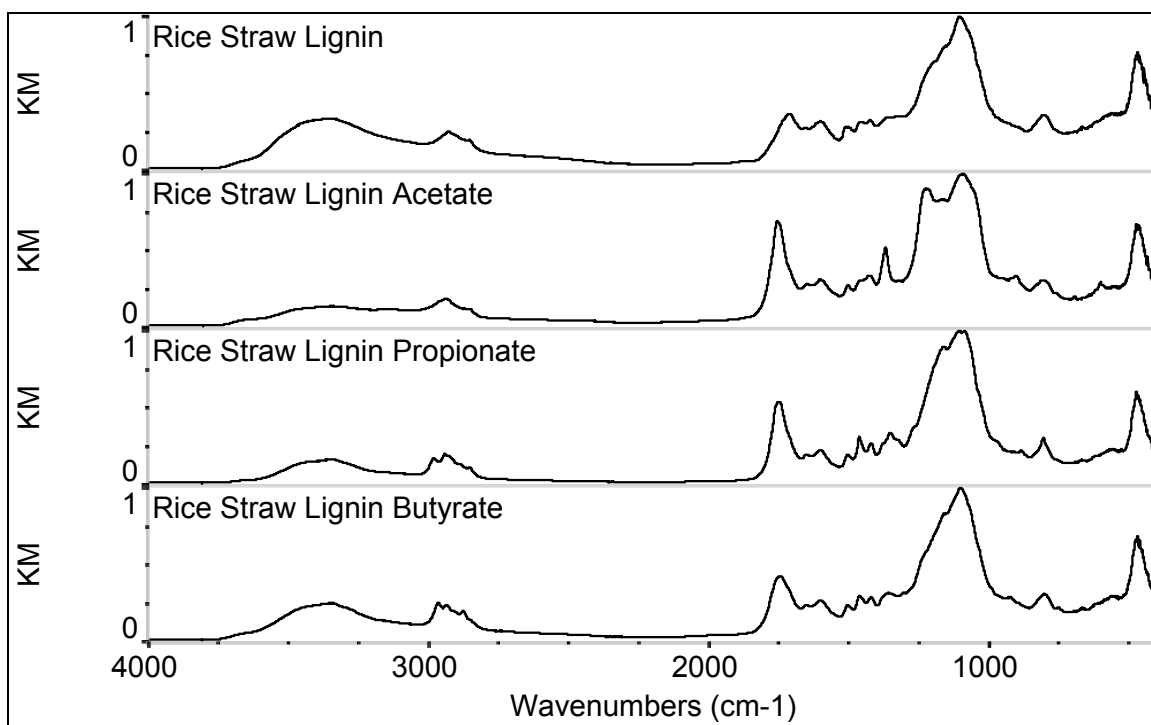
Esterification was expected to increase the solubility of the lignin samples in organic solvents. While kraft lignin esters were readily soluble in a variety of organic solvents (methylene chloride, chloroform, acetone, and tetrahydrofuran), this was not observed for corn stover and rice straw lignin esters. Corn stover esters were only partially soluble in the organic solvents listed above, and rice straw lignin esters were not soluble. For rice straw and corn stover lignin esters, the low solubility could be a function of the high percentage of residual plant polysaccharides (18% and 15%, respectively) still present in the lignin along with its different composition and structure.



**Fig. 7.** Diffuse reflectance FTIR spectra of softwood kraft lignin and its acetate, propionate, and butyrate esters



**Fig. 8.** Diffuse reflectance FTIR spectra of corn stover lignin and its acetate, propionate, and butyrate esters



**Fig. 9.** Diffuse reflectance FTIR spectra of rice straw lignin and its acetate, propionate, and butyrate esters

### Differential Scanning Calorimetry

DSC is an accepted method for determining  $T_g$  of lignin or modified lignin samples (Glasser 2000). The lignin esters were annealed for a period of time several degrees below their expected  $T_g$  to produce more easily discernable transitions on the DSC trace. Without the annealing treatment glass transitions were often difficult to detect, especially in the case of corn stover lignin esters. Glass transitions for rice straw lignin esters were still indiscernible even with annealing. Figures 10, 11, and 12 show DSC thermograms, respectively, of softwood kraft, corn stover, and rice straw lignin esters.

The specific effects of annealing on lignin samples were not investigated. However, its effect on several lignin samples and their  $T_g$ 's has previously been published (Rials and Glasser 1984). Their study indicated that annealing at higher temperatures caused an increase in the  $T_g$  of lignin by a few °C, and longer annealing times of several days caused an increase in enthalpy relaxation.

Work by Glasser and Jain (1993) showed that the  $T_g$  of organosolv lignin esters decreases linearly as the number of carbon atoms in the ester substituent increases. A similar trend was recognized in this study with softwood kraft and corn stover lignin esters, as is shown in Figure 13. The graph also shows that  $T_g$ 's for lignin esters were clearly dependent on lignin type.

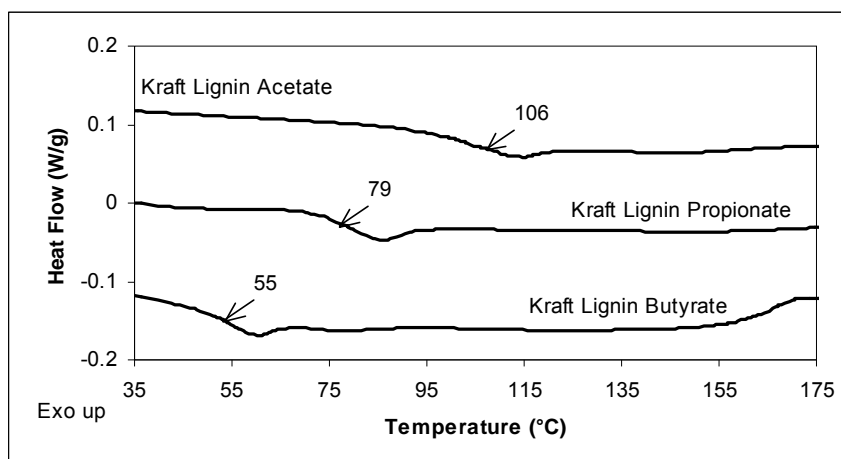


Fig. 10. DSC thermograms of softwood kraft lignin esters with labeled  $T_g$ 's

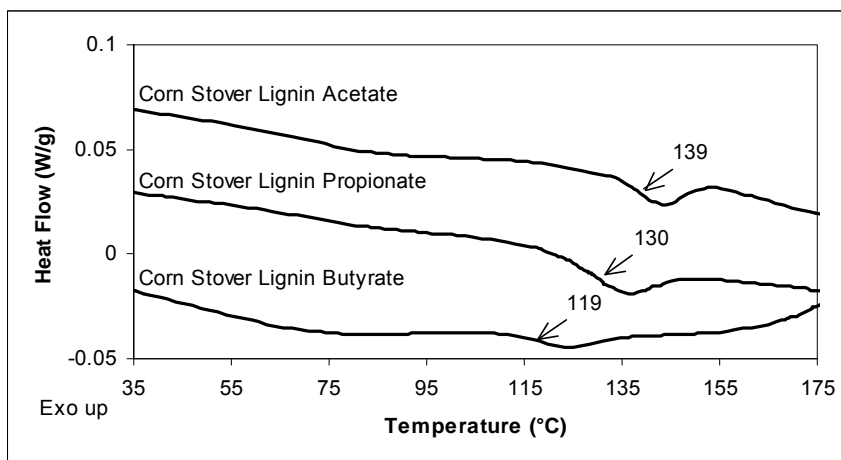


Fig. 11. DSC thermograms of corn stover lignin esters with labeled  $T_g$ 's

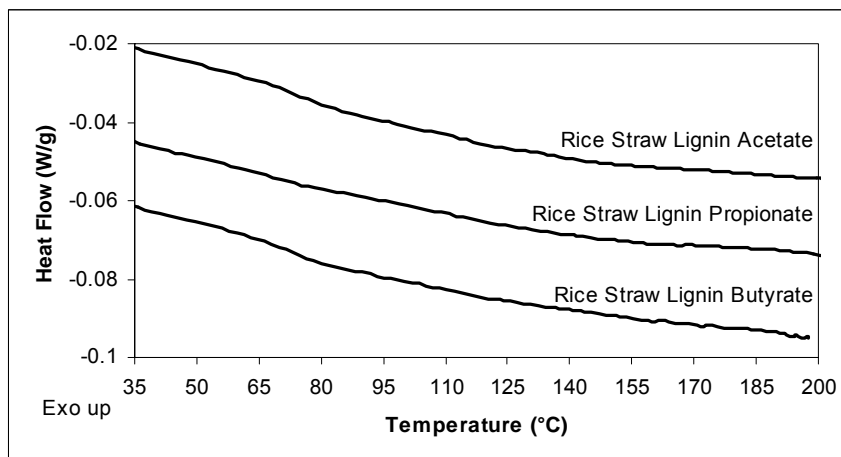
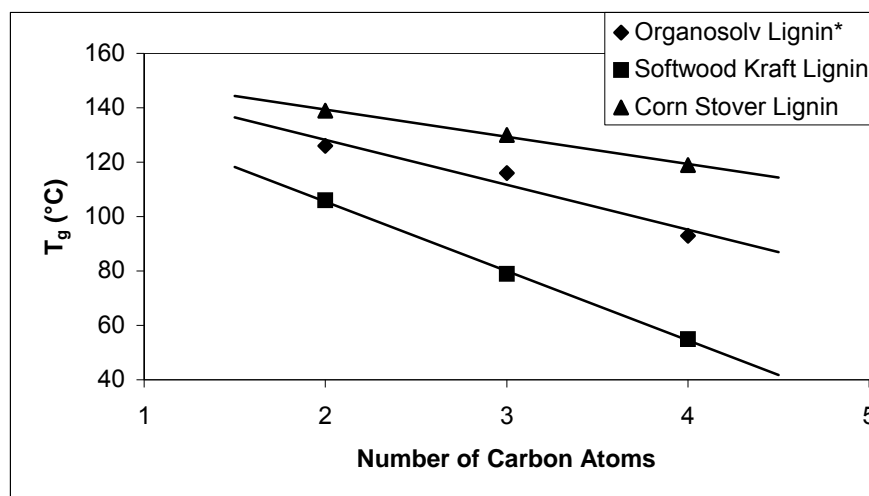


Fig. 12. DSC thermograms of rice straw lignin esters



**Fig. 13.** Relationship between  $T_g$  and number of carbon atoms in each ester substituent for lignin esters. \* Data for organosolv lignin esters is from a study by Glasser and Jain (1993).

### Dynamic Mechanical Analysis

Flexural stress strain curves obtained by DMA showed that the lignin esters had a modulus of elasticity that ranged between 1.7 and 2.4 GPa (Table 3). The flexural modulus was shown to decrease as the length of the ester substituent increased. The flexural modulus values for these lignin esters were comparable to common thermoplastics such as polypropylene (2.1 GPa) and polyethyleneterephthlate (2.3 GPa) (Shah 1998).

DMA provided an alternative method (1 to 2 orders of magnitude) for determining  $T_g$  of the lignin ester samples. The  $T_g$  values determined by DMA can differ by several °C from those by DSC because of the different heating rates (3°C/min versus 5°C/min) applied to each of the methods (Menard 1999). The  $T_g$ 's (defined by the peak of the loss modulus curve) of both corn stover and rice straw lignin esters were readily detectable by DMA (Figs. 14 and 15). Glass transitions for corn stover lignin esters were well defined, characterized by a sharp drop in the storage modulus ( $E'$ ) and relatively narrow peaks in the loss modulus ( $E''$ ) and  $\tan \delta$  curves. Rice lignin ester transitions, however, were not as well defined, characterized by broader  $E''$  and  $\tan \delta$  peaks, and by a more subtle drop in  $E'$ . DMA thermograms of kraft lignin esters were not obtained because of difficulties making sample specimens due to their high brittleness.

### Rheology

Parallel plate rheometry was successfully employed on softwood kraft lignin esters at a frequency of 1 Hz (Fig. 16). However, rheological measurements of corn stover and rice straw lignin esters were impeded by excessive plate slippage, even when serrated plates were used to provide a better grip on the sample. The softwood kraft lignin esters had well defined viscous transitions as the temperature decreased, characterized by a large increase in the complex viscosity ( $\eta^*$ ) and a sharp viscous modulus ( $G''$ ) peak in each system. Figure 16 shows the viscous modulus peaks for softwood kraft lignin acetate, propionate, and butyrate. The complex viscosity 15 °C above the loss modulus

peak maxima was  $6.0 \times 10^4$ ,  $9.5 \times 10^4$ , and  $7.2 \times 10^4$  Pa\*s for kraft lignin acetate, propionate, and butyrate, respectively.

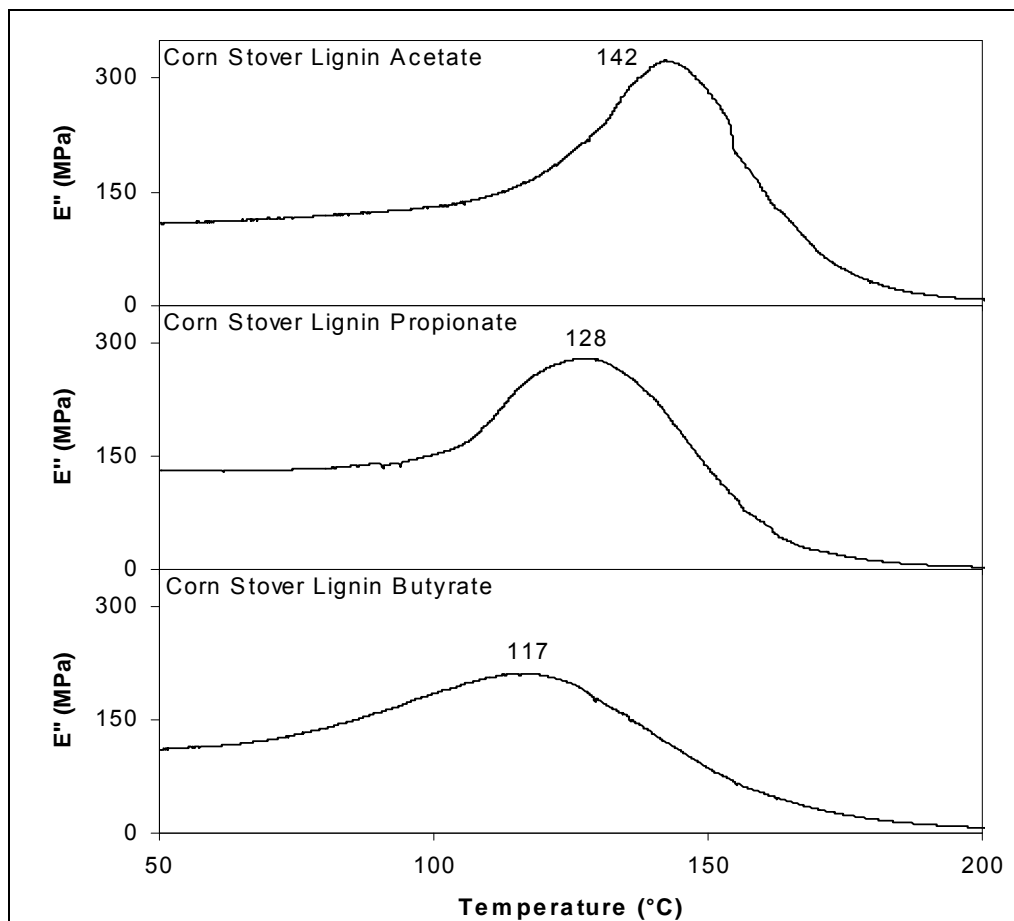


Fig. 14. DMA thermograms of loss modulus ( $E''$ ) of corn stover lignin esters to determine  $T_g$ 's

Table 3. Flexural Moduli of Corn Stover and Rice Straw Lignin Esters

	Ester	Flexural Modulus (GPa)
Corn Stover	Acetate	2.35
	Propionate	1.98
	Butyrate	1.68
Rice Straw	Acetate	2.17
	Propionate	1.87
	Butyrate	1.88



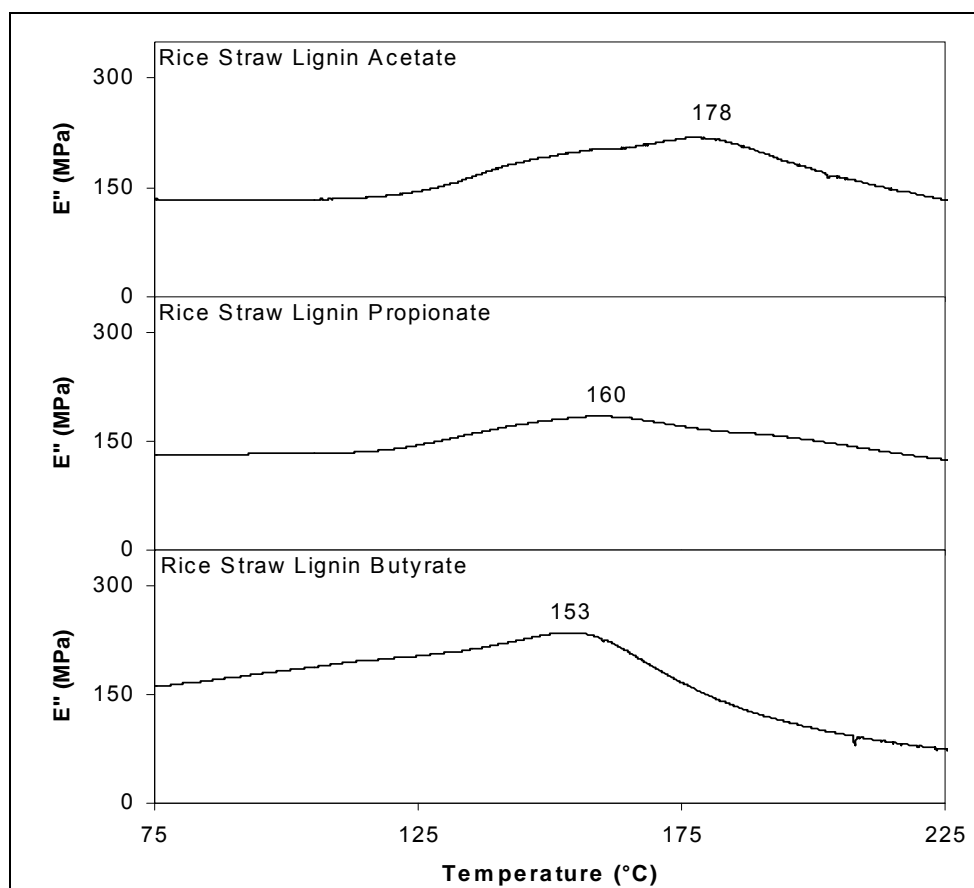


Fig. 15. DMA thermograms of loss modulus ( $E''$ ) of rice straw lignin esters to determine  $T_g$ 's

## CONCLUSIONS

1. Kraft, corn stover, and rice straw lignins were characterized, and detailed analysis showed that the rice straw lignin had a large fraction of residual polysaccharides (< 18%) present, while a smaller fraction was present in the corn stover lignin. Softwood kraft lignin appeared to contain little to no polysaccharides.
2. The origin of the lignin (plant type and isolation process) greatly influences the chemical structure and properties.
3. Derivatives of the various industrial lignins were synthesized successfully in a one-step esterification process.
4. The resultant lignin ester derivatives were shown to have discrete glass transition temperatures. Glass transitions were dependent on lignin type and acyl substituent. The lignin esters showed moderate viscous flow under the rheological conditions tested, suggesting that the lignin-based thermoplastics could be melt processed (molded) into products.
5. The flexural properties of the lignin ester samples were comparable to common plastics such as polypropylene and polyethyleneterephthalate.

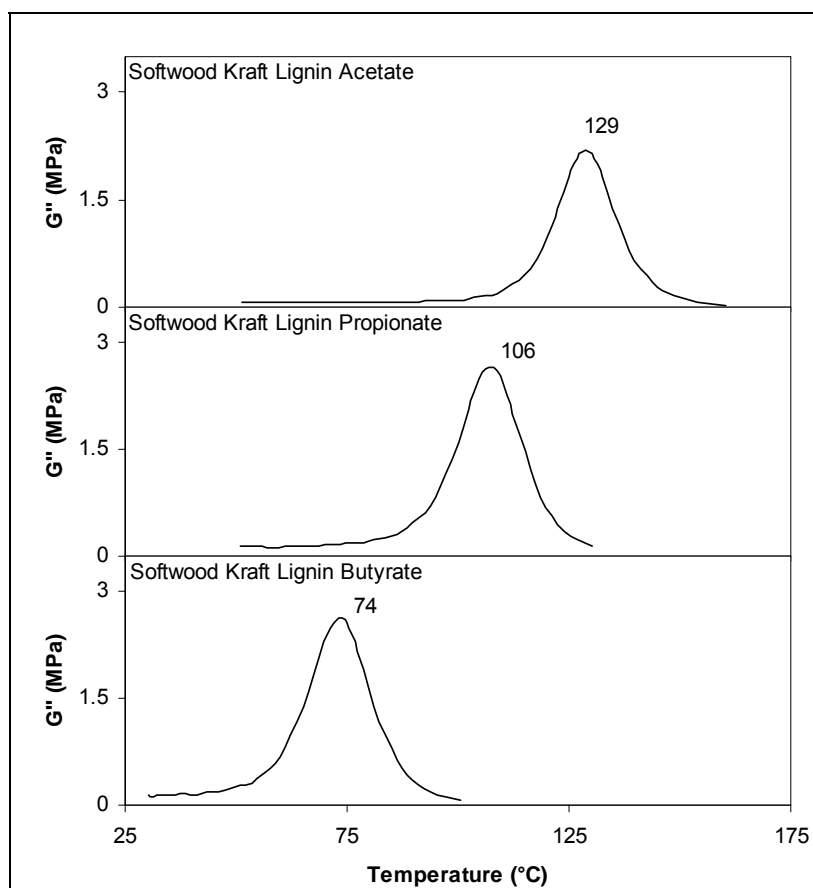


Figure 16: Rheological thermograms showing viscous modulus ( $G''$ ) in softwood kraft lignin acetate, propionate, and butyrate derivatives

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