USE OF LIGNIN SEPARATED FROM BIO-OIL IN ORIENTED STRAND BOARD BINDER PHENOL-FORMALDEHYDE RESINS

Badamkhand Sukhbaatar,[a] Philip H. Steele,[a] and Moon G. Kim[a]*

Bio-oil produced from fast pyrolysis of biomass has been investigated as a renewable fuel and as a source of industrial chemicals. The lignin fraction of bio-oil produced from wood in our fast pyrolysis reactor was separated by using only water and methanol with a 25% yield based on bio-oil weight. This separation procedure appears to be of lower cost than the reported extraction procedure using ethyl acetate as solvent. The isolated pyrolytic lignin was smoothly incorporated into phenol-formaldehyde resins at 30%, 40%, and 50% phenol replacement levels, and the resultant resins were evaluated as oriented strand board core-layer binders. The evaluation results indicated that the pyrolytic lignin is effective for up to about 40% replacement of phenol in synthesizing wood adhesive type PF resins.

Keywords: Bio-oil; Pyrolysis of wood; Pyrolytic lignin; Wood adhesive; Phenol-formaldehyde resins; Oriented strand board binders

*Contact information: a: Department of Forest Products, Mississippi State University, Miss. State, MS 397620-9820. *Corresponding author: mkim@cfr.msstate.edu.* *This article was approved for publication as Journal Article No. FP-512 of the Forest and Wildlife Research Center, Mississippi State University.*

INTRODUCTION

The fast pyrolysis method has been a promising approach to the conversion of biomass materials to liquid bio-oil and gaseous and char products, typically resulting in 75% bio-oil, 13% gas, and 12% char based on the dry wood or biomass weight (Bridgewater 1999). Bio-oils produced from various biomass were found to contain 5-10% organic acids, 5-20% aldehydes and hydroxyaldehydes, 0-10% ketones and hydroxyketones, 20-30% phenolics, and 15-30% water. In all, bio-oils are a mixture of more than 400 chemicals derived from cellulose, hemi-cellulose, and lignin components by thermal breakdown (Diebold and Bridgewater 2002; Czernik and Bridgewater 2005; Ingram et al. 2007).

Bio-oils have been considered as sources of various industrial chemicals (Radelin 1999), and the separation of lignin components has been investigated based on the lignin's good solubility in organic solvents and poor solubility in water (Chum and Black 1990; Chum and Kreibich 1992). The authors first mixed bio-oil with ethyl acetate, and the resultant organic layer was taken up and then washed with water and sodium bicarbonate solutions to extract out water-soluble and organic acid components. The resultant ethyl acetate solution was evaporated to give the pyrolytic lignin in 31% yield based on bio-oil.

The isolated lignin was examined and shown to be satisfactory as a partial replacement of phenol in synthesizing various phenol-formaldehyde (PF) resins,

including novolac and softwood plywood adhesive-type PF resins (Chum and Kreibich 1992). A commercialization effort of the technology was initiated but not continued (Czernik and Bridgewater 2005), possibly due to the costly lignin separation procedure and variable yields of lignin due to the water and sodium bicarbonate washing procedures. Developing a lower cost procedure of separating pyrolytic lignin will help the situation. In this work, the separation of lignin fraction was explored using only water and methanol, and the isolated lignin was evaluated as a partial replacement of phenol in the synthesis of oriented strand board binder-type PF resins.

PF resins are widely used as binders in the manufacturing softwood plywood and oriented strand board (OSB), as well as in other applications in which hot-pressing processes are used. The selection of this binder system is due to the cured PF resins' good binding performance and high exterior durability (Gardziella et al. 2000). Manufacturing of wood adhesive PF resins is geared to fit the hot press bonding requirements for the wood composite boards: hot press curing rate of PF resins becomes faster as the sodium hydroxide content and extent of polymerization attained in resin synthesis are increased. The polymerization extents in resin synthesis results in increasing the resin viscosity, which is controlled to range between 200 cP-500 cP for ease of application, often by increasing the water content of resin in proportion to the polymerization extents. Therefore, the resin cure rate, resin solids level, and sodium hydroxide content of PF resins need to be closely controlled in examining phenol replacement materials (Lee and Kim 2007).

OSB is bonded by hot-pressing of wood mats at 200°C-230°C, using core- and face-layer PF resins as binders, separately, to shorten the hot-press time with minimal over-cure problems in face layers of board. Core-layer binder resin's formulations often involve higher sodium hydroxide content, higher extent of polymerization, and lower resin solids content. Core-layer binder resins are often more critical in that they determine the hot-press time, or the productivity of the plant, and therefore a material for replacement of phenol in wood binder PF resins can be properly qualified by passing the OSB core-layer application test. Current OSB core-layer PF resins are synthesized within a narrow range of parameters: resin solids level of ~50%; sodium hydroxide content of ~5.0%; and urea content of ~5% added as a low cost diluent of solid resin (Kim et al. 1996; Lee and Kim 2007).

PF resins have been generally characterized for viscosity, pH, alkalinity, and resin solids level, as well as for curing rates measured using the dynamic mechanical analysis (DMA) method (Lofthouse and Burroughs 1978; Kim et al. 1991). In the DMA procedure, a piece of fiberglass cloth impregnated with resin is fixed on the two vibrating arms inside a heating chamber, which is then heated in a controlled manner to 140°C-160°C, followed by an isothermal holding for about 10 min. The DMA run results in a measure of stiffness increases of the resin (braid) vs. temperature and elapsed time, from which the curing time and the stiffness of cured resin sample are calculated.

The price of current wood adhesive PF resins is relatively high due to the high price of phenol derived from crude oil. Research on the partial replacement of phenol in PF resins has been carried out with various lignin products derived from sulfite or organosolv wood pulping processes (Sarkanen and Ludvig 1997; Lora and Aziz 1985) and from the wood acid-hydrolysis processes intended for ethanol production (Seller et

al. 1994). These lignin products are of relatively low molecular weights because of breakage of lignin polymers occurring in pulping processes, but they retain phenolic rings that often have one unoccupied ortho-carbon that can react with formaldehyde in the resin synthesis stage. These authors reported that phenol in PF resins can be replaced by lignin at up to 40% with little loss in wood binding performance. However, these lignins are currently not much used as replacement of phenol in industrial manufacturing of PF wood adhesive resins (Seller 1990). Variability of polymer properties of these lignin products appears to be a major problem. The pyrolytic lignin obtainable from bio-oil can be different from the known lignins, and a different lignin separation procedure has required a detailed examination as a phenol replacement in PF resins as an OSB core-layer binder.

Among various wood composite panels, OSB is a good choice to test for the phenol replacement hypothesis. OSB is currently the preferred product for sheathing and decking panels in residential housing construction and has replaced much of the softwood plywood panels traditionally used. OSB is lower in cost because of using low-grade wood, and its performance and durability are comparable to softwood plywood made from high-grade wood. The PF binder resin loading level in OSB is about 4% of dry wood weight, and if the pyorlytic lignin is proved to be useful as a partial replacement of phenol in OSB core-layer binder resin, this implies a relatively large volume potential use in wood adhesive PF resins.

EXPERIMENTAL

Materials

Pine wood bio-oil was produced in an auger reactor at the Department of Forest Products, MSU: the pyrolysis was conducted using dried pine wood particles at 450°C with a resident time of 50s, resulting in the yields of liquid bio-oil in the range of 48.7 to 55.2% based on dry wood weights. Detailed properties of the bio-oil were reported (Ingram et al. 2008). Reagent-grade phenol, urea, and sodium hydroxide were obtained from Aldrich Chemical Company. Formaldehyde aqueous solution (50%) and a commercial OSB face-layer PF resin (RPPB 205C02) were obtained from Georgia-Pacific Resins Plant, Louisville, MS. For laboratory OSB manufacture, wood strands were obtained from Norbord Corp., Guntown, MS. The wood strands consisted of approximately 90% southern yellow pine and 10 % mixed hardwood.

Methods

Exploratory separation of the pyrolytic lignin fraction from bio-oil

The initial objective was to obtain a clean water-insoluble pyrolytic lignin fraction by using water only. Thus, 2325g of pine wood bio-oil was mixed thoroughly with 2400g of distilled water and the mixture was allowed to stand at room temperature for 2h. Then, the water-rich layer was decanted off to give the water insoluble fraction (1160g; 50% yield). A small amount of this lignin fraction was examined by reacting with formaldehyde in the presence of sodium hydroxide according to the formaldehyde

reactivity test procedure (Wooten et al. 1990). The fraction was found in this reaction to give an extensive foaming and phase separation, indicating that it contained certain non-lignin materials that made it unsuitable as a phenol replacement material in synthesizing PF resins. Therefore, the water-insoluble fraction was mixed with methanol in a 1:1 weight ratio to give a clear solution, and then the lignin fraction was precipitated by adding about 1000 g water incrementally while stirring, until no further precipitation of lignin occurred. The mixture was allowed to stand at room temperature to reach a full separation of precipitates, which were collected by decantation, followed by evaporation of methanol on a rotary evaporator at 70°C, yielding 519.0g of dark color viscous lignin material (22.0%).

Determination of formaldehyde reactivity of pyrolytic lignin

The pyrolytic lignin obtained above was evaluated for its reactivity with formaldehyde according to the hydroxylamine hydrochloride method (ISO 9397). Thus, 5.0 g 50% of sodium hydroxide solution, 8.94 g of 50% formaldehyde solution, and 84.0g water were loaded into a stirred reactor. Then, 5.0g of the lignin were added, and the mixture was heated slowly to 60°C. Then, 3.0g samples were taken at 0.5h, 1.2h, and 3.0h of reaction and analyzed for residual formaldehyde contents using the hydroxylamine method (Walker 1964).

^{13}C NMR spectroscopic analyses of pyrolitic lignin and starting bio-oil

^{13}C NMR spectra of the lignin sample obtained above and raw bio-oil were obtained on a Techmag 360 MHz NMR spectrometer at ambient temperature using a 22-µs (80°) pulse-width and 10-s delay time for maximum quantification results (Spectral Data Services, Inc., Champaign, IL). Two grams of samples were dissolved in 1.0 gram of DMSO-d_6 and 400 scans were accumulated and the solvent peak at about 40 ppm was manually eliminated for presentation. Peaks were integrated, and integral values of the two spectra were compared to estimate the characteristics of lignin sample.

Syntheses of OSB core-layer binder PF resins using phenol and pyrolytic lignin

The generally known levels of reagent chemicals for synthesis of PF resins were used for the control PF resin with formaldehyde/phenol ratio of 2.0, NaOH content of 5.0%, resin solids level of 50.0%, and urea content of about 5.0%, as shown Table 1.

The final viscosity values were targeted to be in the range 200cP-300cP, and about 900g of resin were made. Thus, into one-liter reactor equipped with a stirrer, thermometer, and condenser; 264.4g of 99% phenol (2.78 mol), 23.8g of 50% NaOH solution (0.3 mol), and 27.0g distilled water were charged in the given order. The mixture was then heated to 65ºC-70ºC, and 320.5g of 50% formaldehyde solution (5.34 moles) were added in drops to the reaction mixture over a 30-min period while the temperature was maintained. Then, the temperature was increased to 95ºC over a period 25 min and maintained until the reaction mixture reached viscosity I by the Gardner-Holdt (G-H) scale, when the second NaOH solution (28.4g) and water (71.6g) were added. The reaction was then maintained at 85-90ºC until the viscosity reached H-I, and then the third NaOH solution (38.3g) and water (41.9g) were added, and the temperature was maintained in the same range until the viscosity reached N. Cooling of the reaction

mixture was then started and 43.5g of urea, and 40.8g of water were added at about 60ºC and cooled further to room temperature. The finished resin showed JK viscosity by the G-H scale and 250cP by the Brookfield scale.

Table. 1. Material Charges Used in Syntheses of PF Resins with Replacements of Phenol with Pyrolytic Lignin

	Reagents	Conc. (%)	Control Weight (%)	50% Lignin Weight (%)	40% Lignin Weight (%)	30% Lignin Weight (%)
1	Phenol P. lignin	99 100	29.38 0.00	16.49 16.49	18.56 12.37	21.75 9.22
2	NaOH	50	2.64	2.96	2.80	2.76
3	Water		3.00	3.04	7.94	5.25
4	CH_2O	50	35.61	27.90	28.44	30.5
5	Water		7.95	9.25	7.84	8.32
6	NaOH	50	3.16	3.55	3.33	3.31
7	Water		4.65	8.14	4.65	4.87
8	NaOH	50	4.25	1.85	4.47	4.45
9	Water		4.53	5.86	4.77	4.74
10	Urea	100	4.83	4.47	4.83	4.83
	Total		100.00	100.00	100.00	100.00

For syntheses of OSB core-layer resins with partial replacements of phenol with the lignin, the procedure and materials used were the same, except that 30%, 40%, and 50% of the phenol used in control PF resin were replaced with the pyrolytic lignin as shown in Table 1 in percentage values. The amount of formaldehyde was reduced based on the formaldehyde reactivity value determined (0.80 mole formaldehyde/100g lignin). Also, the sodium hydroxide content of synthesized resins were determined by titration, and lignin-modified resins were found to have slightly less than the charged values, apparently due to neutralization with residual organic acids that remained in the lignin fraction used. Therefore, calculated amounts of sodium hydroxide, in comparison with control PF resin, were added to the lignin-modified resins. Nine hundred grams of phenol replaced resins were made, and all resins were stored in a freezer until use.

Measurement of physical and DMA curing properties of resins

Viscosity, pH, nonvolatile resin solids, and alkalinity of all resins were measured according to the standard procedures known in the wood adhesives industry. DMA measurements of resins were carried out on a TA Instruments DMA 983 instrument with a procedure designed to compare the curing rates of different PF resins under the condition similar to the fast temperature increasing schedule used by OSB manufacturing plants. A glass-fiber braid (18.5 x 11.2 x 0.12 mm) was saturated with approximately 0.20 g of resin and clamped horizontally between two sample holding arms. DMA runs were carried out in fixed displacement mode with 0.8 mm amplitude and 1.0 Hz oscillation frequency. The chamber temperature was increased from 30°C at a rate of 25°C/min to 140°C and 160°C, respectively, followed by an isothermal holding for 15 min. From the rigidity development curve, the gel times and cure times of resin were obtained according to a reported procedure (Kim et al. 1991).

Strand board manufacturing procedure

Laboratory strand boards were manufactured with wood strands using synthesized resins as binders of core-layers. Face-layer binder was the commercial resin for all boards. Three-layer, random orientation boards were made with a target density of 0.673 g/cm^3. The resin solids loading level was 4.0%, and the emulsion-type paraffin wax solids level was 1.0% based on dry wood weight for both core-layer and face-layers of boards. Wood strands were first dried to a moisture content of 2%-4% based on dry wood weight, and a calculated amount of wood strands was loaded into a rotating blender. First, the emulsion-type wax was sprayed in using a compressed-air sprayer, and then the binder resin was sprayed in, using a disc-type atomizer spinning at 10,000 rpm, into the rotating blender. Face-layer and core-layer strands were separately blended. Three-layer mats were then made with random orientation of strands with measured weight of resin-applied wood strands in bottom, core, and top layers in 25: 50: 25 weight ratios in a 55.7 cm x 60.7 cm forming box. The mat was pressed in a hot press with an initial platen pressure of 1400 psi and at 220°C. Two press times of 3.0 and 3.5 min were used and duplicate boards were made, with a total of 16 boards by using four synthesized core-layer resins.

Testing procedures of manufactured strand boards

Pressed strand boards were tested according to ASTM D1037 (ASTM 2000) for internal bond (IB), modulus of elasticity (MOE), modulus for rupture (MOR), and 2h and 24h water soak values. Furthermore, 2h-boiled internal bond strengths were determined. Cut test specimens were equilibrated for 2 weeks in a conditioning room set at 7% equilibrium moisture content before the tests. Board densities were measured in the case of specimens prepared for IB and MOR/MOE tests. IB and MOR/MOE strengths were measured on a Tinius Olsen universal testing machine. Boiled IB values of samples were obtained by boiling specimens in water for 2h and drying in an oven for 6h at 103°C, followed by equilibrating to 7% moisture content. Thickness swell (TS) and water absorption (WA) values were measured by soaking specimens (15.2x15.2 cm) in water at room temperature for 2h and 24h.

RESULTS AND DISCUSSION

Pyrolytic Lignin

Separation of lignin from bio-oil using methanol and water

The lignin and neutral fractions of bio-oil are soluble in good organic solvents such as ethyl acetate, while the other components derived from cellulose and hemi-cellulose are much more soluble in water. In one patent (Chum and Kreibich 1992), a combined lignin and neutral fraction was obtained by mixing bio-oil and ethyl acetate, and the ethyl acetate-soluble fraction was taken up and washed with water and sodium bicarbonate solutions to remove organic acids. The ethyl acetate solution was then evaporated to yield lignin, with 30% recovery based on bio-oil weight. A further separation of the neutral components from the lignin fraction was attempted in the patent. The purer lignin fraction thus obtainable will be more suitable for synthesizing PF resins.

In this procedure, the ethyl acetate-insoluble fraction, sodium bicarbonate solution containing organic acid salts, and evaporated ethyl acetate solvent containing volatile bio-oil components were produced. These byproduct materials must be processed in subsequent steps for recovery of solvent and bio-oil components for reuse or further processing. The costs involved in these separation/recovery procedures could be significant. The organic acids remaining in the lignin fraction could complicate the PF resin synthesis reaction due to the neutralization of sodium hydroxide to be added as catalyst for polymerization and curing of resin. However, it is considered that a small amount of remaining organic acids would be tolerated in PF resin syntheses by adjusting the amount of sodium hydroxide level in final resins.

The separation procedure of bio-oil chosen in the present work employed water and methanol in two steps to obtain the water-insoluble pyrolytic lignin fraction. In a typical separation experiment, 2325g of bio-oil was separated using 2400g distilled water in the first step, and then 1000g water and 1000g methanol were used to yield 519.0g lignin (22.0%). Since the starting bio-oil contained about 10% to 15% water, the actual yield amounted to about 25% or more, slightly lower than the yield reported in the ethyl acetate method. In our procedure, the water layer and methanol/water layer, which contain bio-oil components, were produced and needed to be processed in subsequent steps to recover methanol and residual bio-oil components. The lignin fraction may contain some neutral fraction and organic acids, but more washing will be costly. This procedure appears to be of lower cost than the ethyl acetate procedure, but the total amount of water that must be evaporated in the recovery of bio-oil components would be significant. Overall, the current procedure may provide some cost advantage over the ethyl acetate procedure, although details need to be explored further.

Properties of the pyrolytic lignin

The lignin obtained from the water/methanol fractionation procedure contained about 2% methanol and was fluid with a viscosity in the range of 11P. The odor of bio-oil was still apparent but less severe than the raw bio-oil. Filtration of the methanol solution in the procedure allowed elimination of most of the char particles. ^{13}C NMR spectra of the lignin fraction and raw bio-oil in Figs. 1-4, respectively, show various carbon groups spanning the entire spectral region. Peaks were assigned to respective chemical functional group regions according to literature values (Levy and Nelson 1972). The carbon groups were then divided into: aliphatic carbon region (0~49 ppm), aliphatic hydroxyl-carbon region (50~80 ppm); aliphatic dihydroxy-carbon region (81~106 ppm); olefin/aromatic carbon region (107~160 ppm); carboxylic acid carbon region (161~190 ppm); and keto/aldehydic carbon region (191~220ppm). The integral values based on these groupings are reported in Table 2. The NMR data clearly show that much of hydroxyl- and dihydroxyl-carbons of raw bio-oil were eliminated in the spectra of the lignin fraction. Hydroxyl- and dihydroxyl-carbons in bio-oil, derived from cellulose and hemi-cellulose components of wood, are of low in molecular weights and soluble in water and therefore eliminated in the water/methanol separation procedure. Furthermore, only a small amount of methanol, used as lignin separation solvent, remained at about 51 ppm in Fig. 2 at a concentration estimated to be less than 1.0% by weight. The separation procedure also removed much of the carboxylic acid carbons in the 161-190 ppm region.

Table 2. ^{13}C NMR Chemical Shift Ranges and Integral Values of Carbon Groups for Raw Bio-oil and Isolated Pyrolytic Lignin

Chemical shift range (ppm)	0-49	50-80	81-106	107-160	161-190	191-220	Total
Raw Bio-oil: Integral values	45.96	44.58	20.38	82.62	12.89	7.29	213.72
% Concentration	21.50	20.86	9.54	38.66	6.03	3.41	100.00
P. Lignin: Integral values	120.58	18.64	2.00	300.44	7.82	10.00	459.48
% Concentration	26.24	4.06	0.43	65.39	1.70	2.18	100.00

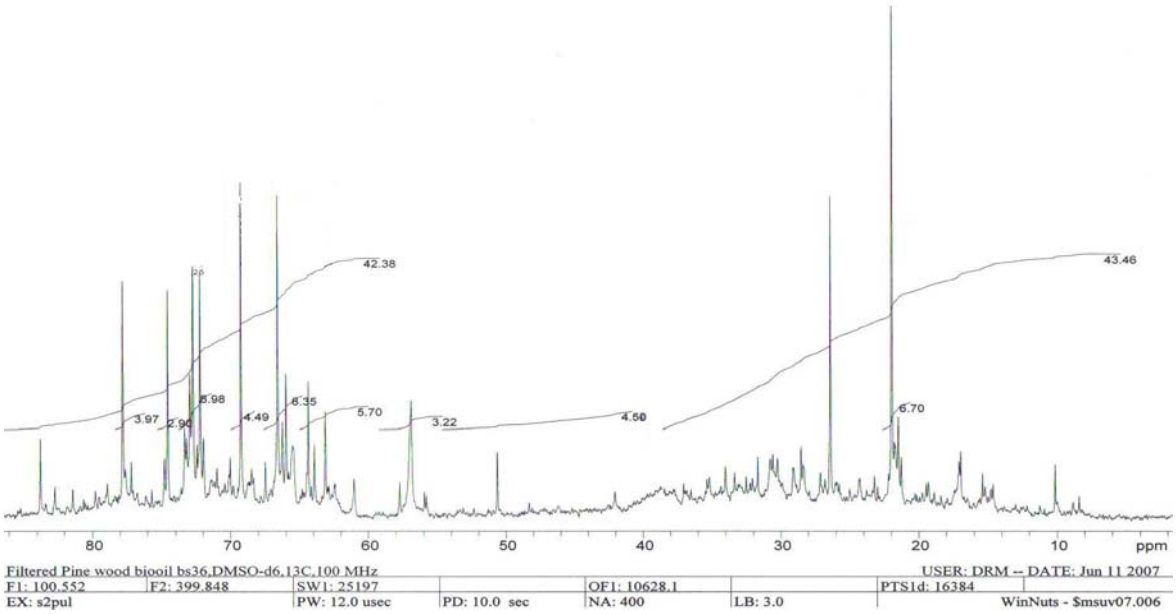

Figure 1. ^{13}C NMR spectrum of raw bio-oil from 0 ppm to 90 ppm with integration values indicated

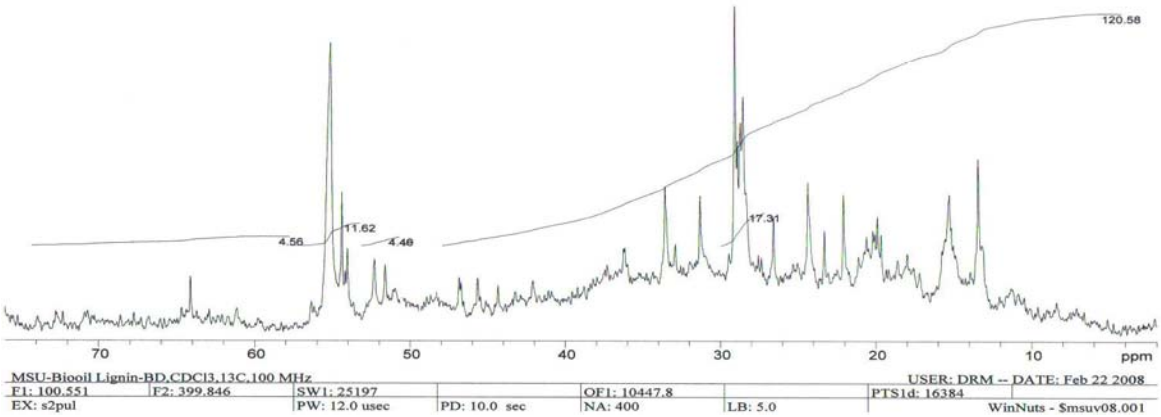

Figure 2. ^{13}C NMR spectrum of pyrolytic lignin from 0 ppm to 80 ppm with integration values indicated

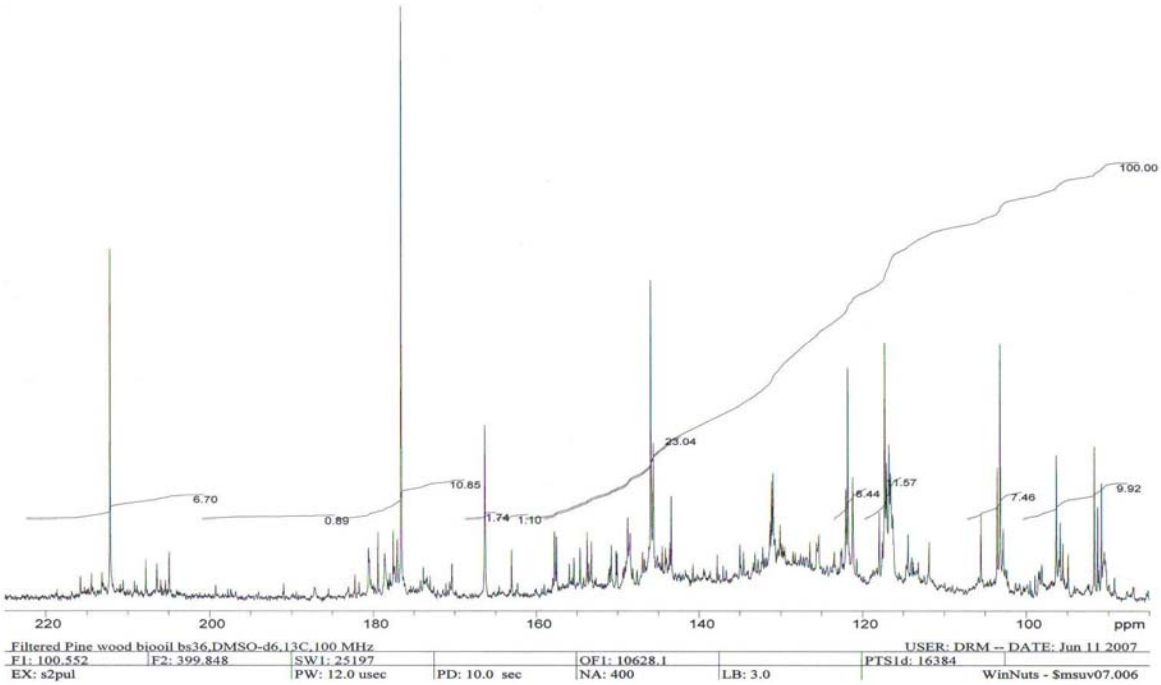

Figure 3. ^{13}C NMR spectrum of raw bio-oil from 80 ppm to 220 ppm with integration values indicated

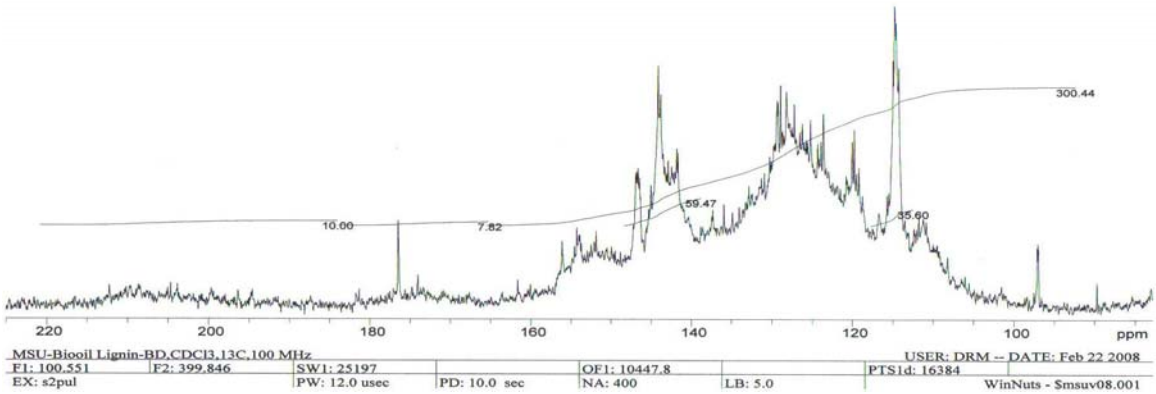

Figure 4. ^{13}C NMR spectrum of pyrolytic lignin from 80 ppm to 220 ppm with integration values indicated

Aliphatic mono- and di-hydroxyl as well as carboxylic acid carbon functional groups in the fractions of lignin are deemed to be unable to participate in the PF resin-forming and curing processes and therefore are considered to be undesirable. The NMR data adequately showed that the water/methanol separation procedure of bio-oil eliminated much of the undesirable components, and the aromatic carbon lignin components were concentrated in the isolated lignin fraction. The formaldehyde reactivity test results of the isolated lignin fraction indicated that about 0.80 mole of formaldehyde reacted with 100 grams of lignin. The formaldehyde reactivity value is slightly lower than values observed for lignin obtained from wood pulping processes (Sellers et al. 1994), but it still indicates potential for a positive contribution when incorporated in PF resins. Overall, the isolated lignin was a dark brown liquid with some bio-oil odor, and the viscosity was in the convenient handling range that is typical for resin raw materials. Small amounts of methanol that remained in the lignin at less than 1.0% would have little effect in manufacturing or curing of resins.

Synthesized Resins as OSB Core-Layer Binders

Resin synthesis procedures

The synthesis procedures for resins with lignin incorporation went smoothly, as with the control PF resin. There was no excessive foaming or phase separation and no difficulty in stirring during the entire procedure. The viscosity measurement was done with a Brookfield viscometer rather than G-H viscometer due to the dark color in the case of lignin-incorporated resins. Therefore, it appears that incorporation of the lignin in PF resins could be done in large scale operations without any handling problem.

Physical properties and DMA curing test results of synthesized resins

Test results of physical and DMA curing properties are reported in Table 3. The resin solids level and alkalinity were carefully adjusted in the resin synthesis procedure to be close to each other, and the adjustments were reflected in the test results. The viscosity values of all synthesized resins were in the similar and spray-able range for common spinning-disc type sprayers. The uniform physical test results of resin solids levels, sodium hydroxide contents, viscosity, etc., assured that the wood composite bonding experiments would display the effects of the lignin added rather than from differences in alkalinity or extent of polymerization.

Table 3. Physical Property and DMA Curing Test Results of Synthesized Resins

Properties	Control PF resin	Pyrolytic Lignin PF Resins		
		30% Lignin	40% Lignin	50%Lignin
Resin solids content (%)	49.6	49.6	49.7	47.4
Alkalinity (%)	4.76	4.76	4.76	4.76
Viscosity (cP)	310	330	450	230
pH	11.94	11.74	11.85	11.80
DMA cure rate at 140°C (min)	14.0	13.5	12..0	10.8
DMA cure rate at 160°C (min)	10.4	11.00	9.6	9.7
DMA modulus cured at 140°C (GPa)	2880	1500	1450	1450
DMA modulus cured at 160°C (GPa)	2500	1950	1450	1470
Free formaldehyde content (%)	~0.0	~0.0	~0.0	~0.0
Modulus: in the shear mode in GPa (GigaPascal).				

Furthermore, the resin physical values were very close to those of commercial core-layer binder PF resins (Seller et al. 1994), so that the evaluation of synthesized resins could be carried out using the commonly used press temperature and press time parameters. The hot-pressing temperature and time parameters in OSB manufacturing determine the productivity of the plant.

The DMA cure rate and cured rigidity strength values in Table 3 reflect the small differences among the synthesized resins arising from the incorporation of lignin. In DMA runs, the rigidity of sample stayed near zero until about 3 min (105°C) and it then started to increase but remained at low values until about 5 min (160°C). Then, the rigidity of sample increased somewhat rapidly, reaching to about 800 GPa at 9.5 min and then very rapidly, reaching a final value of about 2000 GPa at 11.5 min. The rigidity values changed only very slightly during the next 18 min of isothermal run, indicating that the cured resin sample was very stable at the curing temperature. The curing profiles of the lignin incorporated resins agreed well with that of the control PF resin, as well as with data of earlier reports (Lee and Kim 2007). The synthesized resins, however, showed different curing times and different final rigidity values, as shown in Table 3. It is seen that the curing rate of resins became slower, and cured resin rigidity became lower as the lignin content increased, both significantly. The free formaldehyde content for all resins were very small, below the detection limit by the titration method, indicating that the amounts of formaldehyde used in resin syntheses were not in excess and no formaldehyde odor problem will result in using the resins in manufacturing of boards.

Manufacturing and Test Results of OSB

Manufacturing of strand board panels with synthesized resins

In the board mat preparation procedure all synthesized resins behaved well. The spraying of resins on wood strands in a tumbling blender using the common spinning-disc sprayer went smoothly without much build-up of resin in the sprayer or inside the blender drum, indicating that the resins containing the pyrolytic lignin would give no particular rheological problem in general handling and spraying operations such as what can arise from resins having thixotropic characteristics.

One negative characteristic observed in the procedure was the odor of bio-oil for lignin-incorporated resins, but it was relatively mild in general. The resin droplets on wood strands were very uniform on visual inspection, and the resin-loaded strands for all resins were dry to the touch at the time of mat preparation, as is commonly observed with industrial PF resins currently used in OSB manufacturing plants. In this work, the resin-applied wood strands were not oriented in the mat formation, compared to industry processes where strands are oriented to the longer direction of board. The orientation results in better stiffness for board in one direction but has little effects on the internal bond strength. Since internal bond strength values are the key to the evaluation of binder resins, the random orientation used in this work would have served the purpose well.

In the hot-pressing of strand board mats, the press temperature used (220°C) was chosen to be close to the highest temperature used in current OSB industry, and also the press times used (3.0 min and 3.5 min) were the minimum and maximum values used in the industry. The hot pressing of boards went relatively well under the hot-press closing schedule used in this laboratory. However, a few boards shown to experience somewhat high internal gas pressures and five boards out of the sixteen boards showed partial de-laminations. This type of de-lamination commonly arises from factors other than resin curing performances, such as uneven moisture in the mat or pressing speed. These partially delaminated boards were excluded in the calculation of average values except for the 50% lignin resin at 3.0 min press time, where both (duplicate) boards were partially blown and the test data were obtained from un-blown parts of boards.

Table 4. Dry and 2h-Boil Internal Bond Strength and 2h-Boil Thickness Swell

Resin	Press time	Density	Dry Board	2-h Boil /Dry	2-h Boil/Dry	
	Min	g/cm^3	IB (kPa)	IB(kPa)	TS (%)	RS (%)
PF Control	3.5	0.787	578	275	27.3	45.8
	3.0	0.828	707	287	31.8	40.6
30% Lignin	3.5	0.819	682	329	31.8	46.0
	3.0	0.803	582	282	33.8	52.3
40% Lignin	3.5	0.808	570	217	38.7	38.0
	3.0	0.814	657	225	39.6	38.1
50% Lignin	3.5	0.801	510	168	44.2	34.0
	3.0	0.807	459	41	41.2	9.3

TS - thickness swelling; RS - residual strength.

Physical performance test results of prepared strand boards

Physical performance test results of prepared strand boards are reported in Tables 4, 5, and 6, with more detailed data reported in the Master's degree thesis of one of the authors (Sukhbaatar 2008). Density values of prepared strand boards were in a very narrow range of 0.77 to 0.82 g/cm^3, indicating that the resultant IB values could be compared with each other without involving density dependence considerations. The average density values of IB specimens came out to be somewhat higher than the targeted density value of 0.673g/cm^3, which occurred as the result of shrinkage of board thickness after pressing. Overall, however, the comparison of the effects of lignin incorporation in resins on board performances appeared to be unaffected by the slightly higher average board density values.

IB strength test results of dry and 2-h boiled strand boards in Table 4 indicate that the 30%-lignin incorporated resin showed performance values that are comparable with the control PF resin, while the 40%- and 50%-lignin incorporated resins showed gradually decreased dry and 2-h boiled IB strength values. The decreasing trend of IB values with increasing lignin content was also reflected in the 2-h boiled samples' thickness swell values. This result indicates that lignin incorporation of 40% was at the borderline of performance, and 50% lignin incorporation decreased dry IB strength as well as durability of strand board to unacceptable levels. On the other hand, the hot-pressing time of 3.0 and 3.5 min showed no difference in IB strength values, indicating lignin incorporation of up to 40% will have minimal effects on the production rate of strand board. Thus, resins made with 30%-lignin incorporation can be concluded to be as effective as current PF resins in bonding core-layers of strand board, and 40%-lignin incorporation can be made to be comparable with some adjustment of resin synthesis parameters.

Test results of thickness swelling (TS) and water absorption (WA) in Table 5 show that 2-h and 24-h TS and WA values of all three lignin replaced resins were comparable with the corresponding values of the control PF resin. This result indicates that the poor core-layer bonding obtained for the 50%-lignin incorporated resin had little effect on the 2-h and 24h water soak tests. Furthermore, the lignin in the core-layer resins, overall, showed little adverse effect in the water soak tests in comparison with the control PF resins.

Table 5. 2-h and 24-h Water Soak Test Results of Laboratory Strand Boards.

Resin	Press time (min)	2-h Water Soak		24-h Water Soak	
		TS (%)	WA (%)	TS (%)	WA (%)
PF Control	3.5	3.8	7.9	8.3	35.8
	3.0	3.8	8.6	8.6	38.3
30% Lignin	3.5	4.3	7.5	8.0	34.0
	3.0	3.3	7.4	8.7	34.5
40% Lignin	3.5	3.0	7.4	7.2	36.4
	3.0	2.5	7.7	8.9	37.9
50% Lignin	3.5	2.8	6.9	7.8	34.1
	3.0	3.2	7.6	8.9	41.0

The fact that the pyrolytic lignin did not show any more tendency of increased water absorbance in comparison to control PF resin would be an advantage over the commonly available lignosulfonate products, which showed a tendency of somewhat increased water absorption values when used as partial replacements for phenol in PF resins (Sellers et al. 1994).

Test results of modulus of rupture (MOR) and modulus of elasticity (MOE) values in Table 6 indicate that the 30%- and 40%-lignin incorporated resins were comparable to the control PF resin, while the 50%-lignin incorporated resin showed significantly decreased values. Although bending strengths of boards depend much on the bonding quality in the face-layer of board panels, the core-layer bonding of 50%-lignin incorporated resin was significantly poorer and resulted in poor MOR and MOE values.

Table 6. Density and MOR and MOE Values of Laboratory Strand Boards.

Resin	Press time min	Density g/cm^3	MOR MPa	MOE MPa
PF Control	3.5	0.778	23.3	4000
	3.0	0.813	36.2	5500
30% Lignin	3.5	0.775	27.6	5620
	3.0	0.789	28.0	5530
40% Lignin	3.5	0.805	30.4	5900
	3.0	0.798	30.4	4550
50% Lignin	3.5	0.759	24.7	3550
	3.0	0.763	24.9	4090

On the other hand, the 30%- and 40%-lignin incorporated resins can be concluded to have given enough bonding strength in the core layers to have little adverse effects on the bending strength of boards.

CONCLUSIONS

1. The methanol and water separation method of pyrolytic lignin from bio-oil resulted in about 25% yields of lignin fraction based on dry weight of bio-oil. The obtained lignin showed mostly the lignin-like aromatic and aliphatic components in ^{13}C NMR analysis, typical of industrial lignin materials obtainable from wood pulping processes.
2. The isolated lignin was successfully incorporated into PF resins at 30%, 40%, and 50% lignin incorporation levels. The resin synthesis procedures went well without much deviation in comparison to the common synthesis procedure of PF resins.
3. The performance test results of strand boards bonded with control PF and lignin incorporated resins indicated that 30% lignin incorporation will bond strand board core-layer as well as control PF resin and that 40% lignin incorporation would give slightly lower values but can be improved by further research.

4. Resins made with 50% lignin incorporation were found to give inadequate internal bonding strength in the core-layer and unacceptable bending strength values of strand boards.

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