Utilization of Pyrolysis Oil from Pine Wood as Thermosetting Wood Adhesive Resins[*1]

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ABSTRACT

In this study, the possibility of using pyrolysis oil as wood adhesives was explored. Especially, adhesives were formulated by reacting pyrolysis oil and formaldehyde and also partially replacing phenol with pyrolysis oil in phenol-formaldehyde (PF) adhesive and soy hydrolizate/PF adhesive formulation. The pine wood was fast pyrolyized and the oils were obtained from a series of condensers in the pyrolysis system. The oils from each condenser were first reacted with formaldehyde to explore potential use of the oil itself as adhesive. The lap-shear bond strength test results indicated that the oil itself could be polymerized and form bonds between wood adherends. The oils from each condenser were then mixed together and used as partial replacement of phenol (25, 33, and 50% by weight) in phenol-formaldehyde adhesive. The bond strength of the oil containing PF adhesives was decreased as percent phenol replacement level increased. However, no significant difference was found between 25 and 33% of phenol replacement level.

The oil-contained PF resins at 25, 33, and 50% phenol replacement level with different NaOH/Phenol (Pyrolysis oil) molar ratio were further formulated with soy hydrolizate to make soy hydrolizate/pyrolysis oil-phenol formaldehyde adhesive at 6:4 weight (wt) ratio and used for fiberboard manufacturing. Surface internal bond strength (IB) of the boards bonded with 33% replacement at 0.3 NaOH/Phenol (Pyrolysis oil) molar ratio performed better than other replacement levels and molar ratios. Thickness swelling after 24 hr cold water soaking and after 2 hr in boiling water was increased as % replacement of pyrolysis oil increased.

Keywords : adhesive, pyrolysis oil, phenol formaldehyde, soy hydrolizate, fiberboards, bond strength

1. INTRODUCTION

Most of thermosetting adhesive resins used today in the wood industry for building materials depend on petroleum-based chemicals. However, uncertainties in long-term supply of petroleum-derived chemicals and stringent regulations on toxic emissions from building materials

bonded with certain synthetic resins have forced the wood industry to reevaluate the biorenewable resources as alternatives for wood adhesives. One of the most significant challenges in wood industry is to develop adhesive resins from renewable resources meeting performance requirements at reasonable cost.

Carbohydrates and proteins are two components of bio-renewable materials that can be formulated as wood adhesives. Proteins are much more reactive than carbohydrates because amino, carboxyl, aliphatic and aromatic hydroxyl groups provide abundant functionality for chemical crosslinking. Research on protein-based adhesives during the past ten years has largely focused on soy protein, primarily because of its availability and low cost. Kreibich (2000) formulated a cold-setting adhesive for finger-jointing lumber manufactured using the honeymoon system, equal parts of soy protein isolate and phenol-resorcinol-formaldehyde (PRF) resin. A PF-cross-linked soy resin comprising 70% soy flour and 30% PF was also developed by Kuo and co-workers (Kuo et al., 2001). This light-colored soy resin can be used as a liquid resin for exterior plywood or as a powder resin for molded products, but it is not suitable for use as a spray resin. Subsequent research resulted in soy-based adhesives of the same composition, but in a less viscous formulation that can be used as spray resin (Kuo and Stokke, 2001). A similar PF-cross-linked soy resin comprising 30% soy flour and 70% PF also has been developed by Hse and his co-workers for OSB production (Hse et al., 1989).

Recently, fast pyrolysis of biomass draw interest since solid biomass feedstock can be converted into liquid oil that is a complex mixture of various chemicals. These chemicals include phenolics, carbohydrates, organic acids and oligomeric products which has high potential to be used as adhesives (Elder and Soltes, 1980; Die-

bold et al., 1999; Kelly et al., 1997; Pakdel et al., 1994). Elder and Soltes (1980) analyzed pyrolysis oil from pine saw dust and pine bark waste in both quantitatively and qualitatively. They examined the liquid oil by solvent extraction followed by GC/MS and found that the phenolic fraction contained phenol, o-cresol, guaiacol and many other phenolic compounds. They further suggested that single components present in the pyrolytic oil are too low concentration to be isolated as any particular chemical species. Kelly and co-workers (1997) investigated how chemical reactivity of the phenolic-rich fraction and molecular architecture affected properties of phenol-pyrolysis oil resin. The phenolic rich fraction was obtained by neutralization of the pyrolysis oil followed by three-stage mixer settler extraction system using ethyl acetate as organic solvent. They found that the phenolic rich fraction had fewer phenolic hydroxyl group and more methoxyl groups than phenol. The reactivity of the phenolic rich fraction with formaldehyde indicated that the fraction has about half of the reactivity compared to that of phenol. They also reported that the formulated resins compared favorably with commercial PF resin when 25% of phenol was replaced by pyrolysis oil. Chum et al. (1993) developed a process of extracting the phenol/neutral fraction from pyrolysis oil using a solvent extraction technique. Although the prepared resin which replaced 50% of phenol compared well with a commercial PF resin, the lengthy solvent extraction method coupled with a relatively low phenol/neutral fraction yield negative impact on the process economics. Wang et al. (1997) used phenol/neutral fraction from the saw dust pyrolysis oil to replace phenol in PF resin in plywood manufacturing. The lap-shear test on red maple stick indicated that high phenol replacement required longer pressing time to obtain good bond strength in both dry and wet

test. Successful use of whole pyrolysis oil from mixed hardwood up to 50% replacement of phenol also reported (Himmelblau, 1995; Himmelblau and Grozdits, 1997; Himmelblau et al., 2000). The resin was then used to make plywood and the mechanical properties were evaluated. However, viscosity of the formulated resins ranged from 1320 to 6100, which may be too high to apply for the manufacturing of OSB, particleboards, and fiberboards that require spraying of the resin.

Amen-Chen and his co-workers (2002a, b, and c) reported a series of study in order to utilize pyrolysis oil from wood bark residues to replace phenol in oriented strand board (OSB) manufacturing. They synthesized phenol/pyrolysis oil resole resin with different percentage of phenol replacement, formaldehyde to phenol ratio and NaOH to phenol ratio. They synthesized both low and high molecular weight portion for both 25 and 50% phenol replacement level and mixed together before being used because of the phase separation during resin synthesis. Strandboards made with resins with 50% replacement of phenol with pyrolysis oil showed lower wet and dry IB compared to 25% replacement, which may suggest less crosslinking in the 50% replacement resin. They further investigated cure behavior of the resin using differential scanning calorimetry (DSC) (Amen-Chen et al., 2002b). They found that resins containing 50% of pyrolysis oil exhibited slower curing kinetics than commercial resin while resins with 25% pyrolysis oil exhibited almost comparable although not equal. They also reported that at 25% replacement level, the best curing characteristics have been found at formaldehyde to phenolics molar ratio of 1.75 and 2.25 and NaOH to phenolics ratio of 0.25 and 0.35. Addition of small amount of propylene carbonate in 0.5~1.5% range based on resin solid improved the kinetics as well as heat of

reaction of phenol/pyrolysis oil resin although did not significantly improve mechanical properties of panel (Amen-Chen et al., 2002c). Chan et al. (2002) also synthesized phenol/pyrolysis oil resins at different replacement level and used to make homogeneous and 3-layer strandboards. They found that the phenol/pyrolysis oil resins exhibited strong potential to be used as surface resin.

From the above mentioned research, it is clear that pyrolysis oil can be used as replacement of phenol in PF resin system. However, no research on the replacement of phenol in soy protein-PF resin system has been reported. In this research pyrolysis oils were produced from pine wood and the obtained oil was used to partially replace petroleum-derived phenol in PF resin formulation. The overall objectives of this study are thus to explore the potential of using pyrolysis oil from pine wood as partial replacement phenol in soy-PF wood adhesive resins.

2. MATERIALS and METHODS

2.1. Fast Pyrolysis of Biomass

Fast pyrolysis runs were conducted at the pilot plant located in the Biomass Energy Conversion Facility (BECON, Nevada, IA). Pine wood chips were grinded up to 0.5 mm size and air-dried to a moisture content of 2~3% at room temperature. The furnish biomass was placed in the hopper and fed into the fluidized bed pyrolysis reactor with feeding rate of 7~8 kg/h. The pine wood was then pyrolized in the fluidized bed reactor within very short residence time (less than 2 seconds) under nitrogen environment. The operating temperature of the reactor was set at 500°C to maximize oil production. The pyrolized biomass consisted of a mixture of oil, gas and char. Char was first collected at the cyclones while the gas-oil mixture

passed through a series of four condensers (condenser 1 to 4) to be cooled down and precipitated as pyrolysis oil from each condenser. The temperature of the outlet of each condenser was $75 \sim 110$, $38 \sim 40$, $20 \sim 25$, and $15°C$, respectively. The oils not recovered from the condensers were collected at the glass filter located at the end of the system. Pyrolysis oil from condenser 1 was solidified immediately after discharging from the condenser. Therefore, water content, pH, and percent non-volatile of the oils from condenser 2 to 4 were measured. Water content of the oil was measured using Karl-Fischer titration method and percent (%) non volatile was measured by placing 2 g of oil at $105°C$ for 24 hrs. Three replications were made for each measurement.

2.2. Resin Formulation

Adhesive resins were first formulated by reacting pyrolysis oil and formaldehyde to explore potential use of oil itself as adhesive and reactivity of oil from each condensor. Oil from each condenser and paraformaldehyde were loaded into a flask equipped with a reflux condenser and magnetic stirrer. While the mixture was stirred at $65°C$, 50% NaOH solution was added drop-wise over a period of 5 minutes. In addition, water was added to adjust target solid content at 50%. The molecular weight of the pyrolysis oil was assumed and calculated to be the same as that of phenol. Formaldehyde to oil molar ratio and NaOH to oil molar ratio was set at 1.2 and 0.5, respectively. The mixture was initially heated at $65°C$ for 1 hour followed by $95°C$ for 30 minutes.

Resins were also synthesized with phenol and pyrolysis oil from each condenser at 25, 33, and 50% replacement of phenol by pyrolysis oil. For this purpose, pyrolysis oil from each condenser was mixed together. Technical grade

phenol at 90% by weight concentration in water, paraformaldehyde and mixed pyrolysis oil was loaded in a flask equipped with reflux condenser. A 50% NaOH solution was added drop-wise over a period of 5 minutes. Water was also added to adjust target solid content of 50%. Formaldehyde and NaOH ratios to phenol and pyrolysis oil were set at 2.4 (phenol) and 1.2 (pyrolysis oil) and 0.1 (phenol) and 0.5 (pyrolysis oil) respectively. The mixtures were then reacted at $65°C$ for 1 hour followed by $75°C$ for 30 minutes to accomplish partial cross-linking/condensation. They were further reacted at $95°C$ for various times until a target viscosity was reached.

Bonding property of all the formulated resins was evaluated with lap shear test (ASTM D3163-96). Many 180 by 100 by 0.8 mm of wood veneers were prepared and resin was applied at the end most overlap of 12 mm. The resinated lap-shear specimens had 10 minutes of open and closed assembly time respectively. The specimens were then hot pressed at $180°C$ for 5 minutes at pressing pressure of 1.8 MPa. After pressing, the veneers were placed in a conditioning room ($20°C$ 60%RH) for 24 hrs. The specimens were then cut into 25 mm width strip with over-lap area of 300 mm^2. They were tested destructively in lap-shear mode and maximum stress at failure was measured. At least 10 samples were tested for each replacement level.

2.3. Resin Synthesis for Fiberboard

In order to formulate soy protein-based phenolic adhesive resins, soy flour was first hydrolyzed with 8% NaOH and 2% Na_2CO_3 (on dry weight of soy flour) at $140°C$ for 2 hours. Hydrolized soy was then treated with a trace amount of catalyst to enhance cross-linking with phenol/pyrolysis oil resin. Pyrolysis oil contain-

ing PF resins were prepared as mentioned above. The F/P and F/Oil ratio was set at 2.4 and 1.2 but three different NaOH/Phenol (Pyrolysis oil) ratio of 0.1, 0.2, 0.3 for phenol and 0.5, 0.7, and 0.9 for the oil was used. Soy hydrolyzates and phenol/pyrolysis oil resin were then mixed at 60 : 40 (solids to solids) weight ratio at 50°C for 30 minutes with mechanical stir. The resins were then cooled down and sprayed on the wood fiber in a tumbler spraying system. The resinated fibers were manually formed in to a mat. The formed mat was then hot pressed in a 150-ton hydraulic press for set amount of time.

The MDF was made according to the following specifications:
- Replication: 2 boards
- Fiber furnish: thermomechanical softwood (*pinus* spp.) fibers.
- Resin content: 12% based on dry weight of fiber
- Resin type: Soy hyrolyzate (60%) and Phenol/pyrolysis oil formaldehyde (40%)
- Board size: 381 by 381 by 127 mm
- Target density: 0.75 g/cc
- Press temperature: 200°C
- Press time: 8 minutes

Boards were made for each resin treatment, with two boards in each batch. Control boards were also made with only soy hytrolyzates/PF adhesive.

Immediately after pressing, boards were stored at 105°C for 12 hrs for the post-treatment followed by conditioning at 65% RH and 20°C environment for 1 week. They were then trimmed to 356 by 356 mm to measure overall board density. Boards were then cut into series of smaller specimens to evaluated modulus of rupture (MOR), modulus of elasticity (MOE), and internal bonding (IB) strength in accordance

with ASTM D 1037-99a. Percent thickness swelling (TS) after 24 hr in cold water and 2-hr in boiling water was also measured. Results were analyzed to determine the effects of biomass type and phenol replacement ratio with pyrolysis oil on product performance.

3. RESULTS and DISCUSSION

3.1. Characterization of Pyrolysis Oil

From the fast pyrolysis of pine wood, yields of pyrolysis oil, char and gases were 62.2%, 8.7% and 27.6%, respectively. The pyrolysis system used in this study was unique in terms of oil production. Oils were obtained such that the oils produced by fast pyrolysis passes through a series of four condensers run at different temperatures. The oil produced by the fast pyrolysis was first collected at condenser 1 followed by 2, 3, and 4. Therefore the yield and properties of the oil from each condenser was different. The oil from condenser 1 was solidified immediately after it comes out form the condenser that had an exit temperature of 90~110°C. The rest of the oils obtained from condenser 2, 3 and 4 were liquid. Although the amount of oil caught at the glass filter was substantial, it was difficult to recover the oil and thus not recovered or used in this study. The yield of oil from each condenser was 12.2%, 27.1%, 9%, and 11.6% (from condenser 1 to 4).

Table 1 shows the water content, percent non-volatile, and pH of pyrolysis oil recovered from each condenser. The oils from condenser 3 has highest water content and lowest percent non-volatile while those from 4 has lowest water content and highest percent non-volatile. The pyrolysis oils are highly acidic with pH ranges from 2.2 to 2.6, which may be attributable to the organic acids in the oil.

Table 1. Water content, % non-volatile, and pH of pyrolysis oil from pine wood

Biomass	Condenser	% yield[1]	Water content (%)[2]	% non-volatile[3]	pH
	1	12.2 (1.4)	N/A	97.8 (1.2)	N/A
	2	27.1 (2.1)	19.3 (1.5)	49.3 (3.7)	2.6
Pine	3	9.0 (0.6)	41.7 (2.5)	27.0 (2.1)	2.2
	4	11.6 (1.4)	13.8 (0.9)	59.4 (4.6)	2.5
	Glass Filter	40.1 (3.8)			

[1,2] and [3] : Number of replicates: 3
Numbers in the parenthesis are standard deviations

3.2. Bond Strength of Pyrolysis Oil and the Oil Containing PF Resin

When pyrolysis oils obtained from condenser 2 and 4 was reacted with formaldehyde under alkaline condition, phase separation was observed. Liquid part resided on top and more viscous part resided at the bottom. Amen-Chen and his co-workers (2002) also reported phase separation at 100 (pyrolysis oil alone) and 75% oil replacement level. This could be due to the low solubility of some high molecular weight components in the pyrolysis oil from condenser 2 and 4. Lap shear test for this resin was performed for both liquid and viscous fractions and no attempts was made to homogenize the separated phases. The test results are shown in Fig. 1.

From the Fig. 1, the bond strength of the resins made from the oils from condenser 2 and 4 was generally higher than that of the resins made from condenser 3. In addition, bond strength of viscous fraction of the resin from condenser 2 and 4 oils were much higher than liquid fraction. This could be due to the low reactivity and solid content of the oil from condenser 3 and liquid fractions of resins from condenser 2 and 4. Especially, the viscous fraction of the oil-formaldehyde resins made with oils from condenser 2 had highest bond strength. From the test, it could be speculated that the viscous fraction contained more phenolic com-
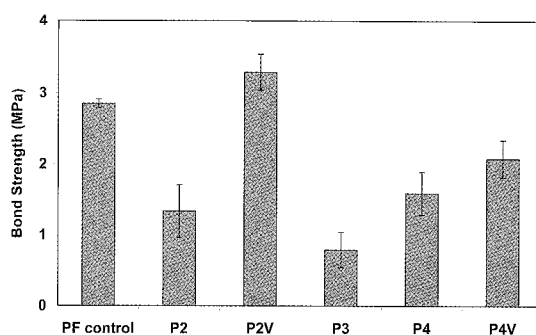

Fig. 1. Lap shear bond strength of pyrolysis oil-formaldehyde resin (P2: liquid part of adhesives made from condenser 2, P2V: viscous part of adhesives made from condenser 2, P3: pyrolysis oil adhesives made from condenser 3, P4: liquid part of adhesives made from condenser 4, P4V: viscous part of pyrolysis oil adhesives made from condenser 4).

pounds which could participate in chain building. The results indicate that the pyrolysis oil alone could be formulated as wood adhesives. Although the resins made with oils from condenser 2 and 4 performed better than those from condenser 3, they were mixed together so that the whole liquid fraction of the obtained oils was used as a partial replacement of phenol in PF resins and soy hydrolizate/PF adhesives.

The lap shear test result for the resins made with phenol/pyrolysis oil at 25, 33, and 50% phenol replacement level was shown in Fig. 2. The lap shear bond strength of PF adhesives containing pyrolisys oil decreased as % replacement of phenol increased. Compared to control
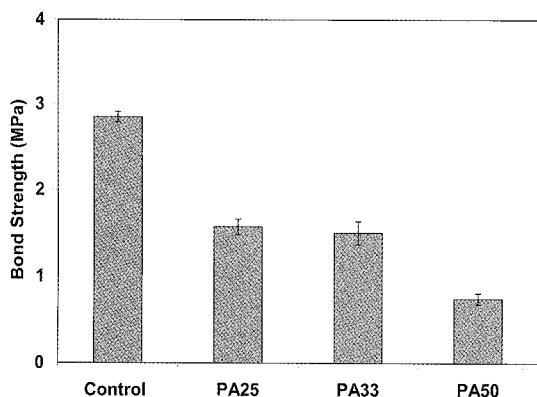
Fig. 2. Lap shear bond strength of soy hydrolizate/ pyrolysis oil-PF adhesives (PA25: 25% phenol replacement level, PA33: 33% phenol replacement level, PA50: 50% phenol replacement level).

PF resin, the bond strength was significantly reduced at low (25%) phenol replacement level. However, there was no significant difference in bond strength between 25 and 33% replacement level. When the replacement level increased to 50%, bond strength again considerably decreased. No phase separation was observed at all phenol replacement level.

3.3. Properties of Fiberboard Made with Soy Hydrolizate/Pyrolysis Oil-PF Adhesives

Formulated phenol/pyrolysis oil resins were further reacted with soy hydrolizate (40 : 60) and used for fiberboard manufacturing. Unfortunately, most of fiberboards had internal blow. This suggests that residual stress of densified fibers and internal gas pressure may be larger than the bond strength between wood elements by adhesive curing. Therefore, the restraint provided from the platen is removed, in other words, when press opens, failure between fiber elements occurred. In order to optimze the hot pressing condition to prevent internal blow, fur-

ther investigation may be necessary. The soy hydrolizate/pyrolysis oil-PF resins may require higher pressing temperature or longer pressing time to be used in board manufacturing or it could be used as a face resin (Kuo and Stokke, 2000).

Since most of the fiberboards had blow at the mid-thickness, internal bond strength were measured only on the one half thickness of the IB specimens and was called surface IB. The surface IB may be different from the standard IB but this also provides useful information on how much bond strength developed at a certain hot pressing condition. Thickness swelling was also measured for both after 24 hour cold water soaking and 2 hour boiling. The results were summarized in Table 2.

At 25% replacement level, surface IB was slightly increased as NaOH/Phenol molar ratio increased from 0.1 to 0.2 but significantly reduced as NaOH/Phenol molar ratio increased to 0.3. However, at 33% replacement level, surface IB was decreased as NaOH/Phenol molar ratio increased from 0.1 to 0.2. But, the surface IB was considerably increased as NaOH/Phenol molar ratio increased to 0.3. At 50% replacement level, surface IB tended to increase as NaOH/Phenol molar ratio increased. Highest surface IB value of 25% phenol replacement level was obtained at NaOH/Phenol molar ratio of 0.2 while at 33% level, the ratio increased to 0.3. However, the highest surface IB values of 33% phenol replacement level were higher than that at 25%. At 50%, the highest surface IB values were obtained at NaOH/Phenol ratio of 0.3 but the value was lower than those at 25 and 33%.

The thickness swelling after 24 hr cold water soaking test and 2 hr boiling test results indicated that as % phenol replacement level increased, more % thickness increase were observed. Especially at 50%, the boards were dis-

Table 2. Mechanical and physical properties of fiberboard bonded with soy hydrolizate/pyrolysis oil-PF resin

Phenol replacement level	NaOH/ Phenol molar ratio	pH[1]	Solid content[2] (%)	Viscosity (cPs)	Board density (Kg/m³)	Surface IB (MPa)[3]	Thickness swelling (%)[4]	
							24 hr cold water soaking	2 hr boiling
25	0.1	9.02/9.50	48.7/39.3	20	752	0.27 (0.03)	13.5 (1.1)	71.4 (10.5)
	0.2	9.45/9.5	50.3/40.6	20	758	0.33 (0.08)	14.1 (1.2)	54.3 (6.8)
	0.3	9.85/9.75	47.1/40.6	65	744	0.19 (0.02)	27.7 (1.2)	66.3 (8.4)
33	0.1	8.97/9.36	52.2/40.7	20	752	0.31 (0.03)	18.4 (1.6)	126.5 (18.8)
	0.2	9.35/9.27	53.1/41.0	60	748	0.27 (0.03)	14.8 (1.2)	91.8 (10.3)
	0.3	9.75/9.74	51.3/40.7	60	758	0.40 (0.02)	18.1 (1.3)	97.4 (10.1)
50	0.1	9.15/9.55	53.2/39.3	55	757	0.26 (0.05)	125.6 (13.4)	Fail
	0.2	9.62/9.25	53.4/41.7	65	750	0.27 (0.04)	122.6 (16.8)	Fail
	0.3	9.77/9.72	50.3/40.5	55	753	0.29 (0.04)	87.3 (8.8)	Fail
Control		9.85	50.1/40.2	55	751	0.47 (0.02)	6.1 (1.0)	24.7 (2.2)

[1] pH of oil containing PF resin/pH of oil containing PF-soy hydrolizate resin
[2] Solid content of oil containing PF resin/ solid content of oil containing PF-soy hydrolizate resin
[3] number of replicates: 10
[4] number of replicates: 5
Numbers in the parenthesis are standard deviations

mantled after 2 hr boiling test and unable to measure thickness swelling.

4. CONCLUSION

The pine wood pyrolysis oil was used to partially replace phenolic portion of soy hydrolizate/PF adhesive. The adhesives formulated only with the pine wood pyrolysis oil and formaldehyde was first synthesized. When synthesizing adhesives with pyrolysis oil from condensers 2 and 4, phase separation was observed. The lap-shear test of the adhesives indicated that the viscous part of adhesives made with pyrolysis oil from condenser 2 performed better than those from other condensers. The oil containing PF adhesives were also prepared at 25, 33, and 50% phenol replacement level using mixed pyrolysis oils. Lap shear test results indicated that there was no significant difference in bond strength between 25 and 33% phenol replacement level. However, at 50% replace-

ment, bond strength was significantly reduced. PF/pyrolysis oil adhesives containing 25, 33, and 50% of pyrolysis oil were further reacted with hydrolyzed soy at soy/pyrolysis oil-PF weight ratio of 6 : 4. The adhesives were used for manufacturing fiberboards. Despite internal blow in the fiberboard, surface IB and thickness swelling were measured. All fiberboards manufactured with adhesives having 25, 33, and 50% of phenol replaced by pyrolysis oil exhibited lower IB than control. At 25 and 33% replacement level, highest surface IB values obtained at NaOH/Phenol molar ratio of 0.2 and 0.3 respectively. Thickness swelling after 24 hr water soaking and after 2 hr boiling water was increased as % replacement of pyrolysis oil increased. These preliminary results indicate that pine wood pyrolysis oil could be used to replace up to 33% of phenol in soy hydrolizate/PF adhesive for the fiberboard manufacturing. However, when used in fiberboard manufacturing, the adhesive may require higher

pressing temperature and longer pressing time, which makes them more suitable for the face resin of the boards. Further characterization of pyrolysis oil, formulating pyrolysis oil containing PF/soy hydrolizate resins under various NaOH/Phenol, F/P ratios, as well as soy hydrolizate/PF weight ratio followed by board manufacturing condition and characterization of manufactured board may be necessary to use the adhesive in the wood-based composite manufacturing.

REFERENCES

1. Amen-Chen, C., B. Riedl, X.-M, Wang, and C. Roy. 2002a. Softwood bark pyrolysis oil-PF resols. Part1. Resin synthesis and OSB mechanical properties. Holzforschung 56: 167~175.
2. Amen-Chen, C., B. Riedl, and C. Roy. 2002b. Softwood bark pyrolysis oil-PF resols. Part2. Thermal analysis by DSC and TG. Holzforschung 56: 273~280.
3. Amen-Chen, C., B. Riedl, X.-M. Wang, and C. Roy. 2002c. Softwood bark pyrolysis oil-PF resols. Part3. Use of propylene carbonate as resin cure accelerator. Holzforschung 56: 281~288.
4. American Society for Testing and Materials. 1999. Standard test methods for evaluating properties of wood-based fiber and particle panel materials. ASTM Standard D-1037. ASTM. West Conshohocken, PA.
5. Chan, F., B. Riedl, X.-M. Wang, X. Lu, C. Amen-Chen, and C. Roy. 2002 Performance of pyrolysis oil-based wood adhesives in OSB. Forest Products Journal 52(4): 31~38.
6. Chum, H., J. Diebold, S. Black, and R. Kreibich. 1993. Resole resin products derived fro fractionated organic and aqueous condensation made by fast pyrolysis of biomass materials. U.S. Patent No. 5, 235, 021.
7. Diebold, J. P., T. A. Milne, S. Czernik, A. Oasmaa, A. V. Bridgewater, A. Cuevas, S. Gust, D. Huffman, and J. Piskorz. 1999. Proposed specifications for various grades of pyrolysis oils. In proc. 4th Biomass Conference of the Americas.

Oakland, CA. pp. 433~447.
8. Elder, T. J. and E. J. Soltes. 1980. Pyrolysis of lignocellulosic materials. Phenolic constituents of a wood pyrolytic oil. Wood and Fiber Science 12(4): 217~226.
9. Himmelblau, D. A. 1995. Phenol-formaldehyde resin substitutes from biomass tars. In Wood Adhesives 1995. Forest Products Society, Madison, WI. pp. 155~162.
10. Himmelblau, D. A. and G. A. Grozdits. 1999. Production and peformance of wood composite adhesives with air-blown fluidized-bed pyrolysis oil. In proc. 4th Biomass Conference of the Americas. Oakland, CA. pp. 541~547.
11. Himmelblau, D. A., G. Grodits, and M. D. Gibson. 2000. Performance of wood composite adhesives made with biomass pyrolysis oil. In Wood Adhesives 2000, Forest Products Society, Madison, WI. pp. 133~139.
12. Hse, C. Y., F. Fu, and B. S. Bryant. 2001. Development of formaldehyde-based wood adhesives with co-reacted phenol/soybean flour. In Wood Adhesives 2000, Proc. No. 7252, Forest Products Society, Madison, WI.
13. Kelley, S. S., X.-M. Wang, M. D. Myers, D. K. Johnson, and J. W. Scahill. 1997. Use of biomass pyrolysis oils for preparation of modified phenol formaldehyde resins. In proc. Developments in thermomechanical biomass conversion. Blackie& Professional. London, New York, Tokyo. pp. 557~572.
14. Kreibich, R. 2000. personal communication.
15. Kuo, M. L., D. J. Myers, H. Heemstra, D. G. Curry, D. O. Adams, and D. D. Stokke. 2001. Soybean-based wood adhesives and wood composites bonded with these resins. US Pat. 6, 306, 997.
16. Kuo, M. L. and D. D. Stokke. 2001. Soybean-based adhesives for composite products. In Wood Adhesives 2000, Proc. No. 7252, Forest Products Society, Madison, WI.
17. Pakdel, H., G. Zhang, and C. Roy. 1994. Detailed chemical characterization of biomass pyrolysis oil, Polar fractions. Advances in Thermochemical biomass conversion Vol. 2. A.V. Bridgewater, ed. Blackie Academic, Glasgow, Scotland. pp. 1068~1085.

18. Wang, X.-M., M. D. Myers, and S. S. Kelly. 1997. Mechanical properties of wood composites made from biomass-derived phenol-formaldehyde resins. In: Proceedings of the 31th International Particleboard/Composite Materials Symposium. Eds. M.P. Wolcott, L.C. Miklosko. Pullman, WA., U.S.A. pp. 199.