

# Effect of *Pinus radiata* Bark Polyphenols on Phenol Liquefaction of Cellulose in the Presence of *p*-Toluene Sulfonic Acid Catalyst

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## Abstract

The influence of *Pinus radiata* bark polyphenol components in the phenol liquefaction of *P. radiata* bark was investigated using *p*-toluene sulfonic acid (PTSA) and sulfuric acid (SA) as acid catalysts. A series of the phenol liquefaction reactions were carried out using mixtures of pure cellulose with increasing amounts of hot-water extract (HWE) of *P. radiata* bark—the polyphenol-rich component of bark. The yields of liquefied product reactions and combined phenol amounts in them were determined, and the liquefaction residues were also analyzed for determination of acid-soluble and insoluble polyphenols and residual cellulose fractions.

The yield of cellulose liquefaction decreased linearly with increasing amounts of HWE with the effect being more pronounced for SA than for PTSA. The combined phenol amount increased with liquefaction yield increases for both SA and PTSA catalysts, but at liquefaction yield levels above 83 percent, more phenol was combined for SA catalyst than for PTSA catalyst. The liquefaction residues contained lower cellulose and higher polyphenol components for SA catalyst than for PTSA catalyst at the same liquefaction time. The results indicate that the bark polyphenol components can significantly interfere in the acid-catalyzed bark phenol liquefaction reactions by their excessive condensation with cellulose and/or phenol, especially in the presence of SA catalyst.

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*P. radiata* wood is a major importing wood in Korea for production of lumber, medium-density fiberboard, and pulp and paper, and huge amounts of bark are discharged as wastes from these wood-processing industries. Although bark is an abundant source of various polyphenols, it has been used mostly as boiler fuels for generation of energy. *P. radiata* bark is known to contain about 55 percent polyphenols by weight with the major component consisting of proanthocyanidins having the flavan-3-ol repeating units linked mainly through C4–C8 (or C6) bonds (Ku and Mun 2007, Ku et al. 2007).

Acid-catalyzed phenol liquefaction of lignocellulosic biomass, such as wood and bark, is a well-known method (Alma et al. 1995a, 1995b, 1998; Hassan and Mun 2002; Mun et al. 2002, 2006; Mun and Jang 2009) with the resultant liquefied products being reported to be useful as raw materials for polymeric resins for moldings and wood adhesives (Santana and Baumann 1996, Alma et al. 2000, Lee 2003, Hassan et al. 2009, Wang et al. 2009, Zhao et al. 2010). Sulfuric acid (SA) is a typical catalyst for the phenol liquefaction and is usually used in the range of 2 to 8 percent

based on the liquefying agent. However, when SA catalyst was used for phenol liquefaction of *P. radiata* bark, which contains a high amount of polyphenols such as proanthocyanidins, the liquefaction reaction rate was reported to be significantly slower than wood, especially at the low phenol-to-bark ratio of about 2 (Mun et al. 2006). The slow phenol liquefaction rate of pine bark with mineral acid catalysts, such as SA or hydrochloric acid, especially at low phenol-to-bark ratios, has led to investigation of various organic

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Forest Prod. J. 62(3):234–239.

sulfonic acids, such as methane sulfonic acid, naphthalene sulfonic acid, benzene sulfonic acid, and *p*-toluene sulfonic acid (PTSA), and a markedly higher effectiveness was reported in comparison with SA catalyst (Mun et al. 2002, 2006). PTSA has also been used by Jasiukaitytė et al. (2009) as a catalyst for cellulose liquefaction in ethylene glycol. When the phenol liquefaction process with organic sulfonic acids was applied to cellulose substrates, contrary to our expectation, all the liquefaction rates were lower than those carried with SA catalyst at various liquefaction temperatures in spite of similar activation energies observed for both catalyst types (Mun and Jang 2009). Therefore, the objective of this study was to clarify the different roles of SA and organic sulfonic acid catalysts in the phenol liquefaction of pine bark and cellulose. To simplify the experiment by excluding the influence of other pine bark components, such as lignin and hemicellulose components, we carried out model phenol liquefaction reactions using various mixtures of cellulose and hot-water extract (HWE) of *P. radiata* bark as liquefaction substrates. Liquefaction yields and combined phenol amounts were determined, and liquefaction residues were further analyzed to investigate the direct condensation reactions that are possible to occur between cellulose and polyphenol components. Also, we analyzed the present results in conjunction with the results obtained from the similarly carried out phenol liquefaction reactions of raw *P. radiata* bark reported in the previous work (Mun et al. 2006).

## Materials and Methods

### Materials

Whatman filter paper (No. 2) was used as cellulose substrate, cut into 0.5 by 0.5-cm pieces. *P. radiata* bark was provided by Sawmilling Co. Ltd. located in Christchurch, New Zealand. The bark was dried in a convection oven at 60°C ± 1°C for 48 hours and ground in a Wiley mill, and the 20- to 80-mesh-size bark powder collected was used for this study. All chemicals were reagent grades obtained from commercial suppliers.

### Preparation of HWE of pine bark

The bark powder (600 g, oven-dried [o.d.] weight basis) was extracted with 6 liters of deionized (DI) water at 100°C by occasional stirring for 1 hour, followed by filtering through a cartridge with a 3-μm-pore-size filter. The filtrate was evaporated on a large-scale rotary vacuum evaporator (N-12; Eyela, Tokyo, Japan) at 60°C to an approximately 2-liter volume, followed by freeze-drying, and then the residues were dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>, yielding 120 g of reddish brown powder, HWE.

### Acid-catalyzed phenol liquefaction procedure of cellulose and HWE mixtures

The model liquefaction procedure was carried out basically following our previously reported acid-catalyzed phenol liquefaction procedure of *P. radiata* bark, wherein 2.5 g of bark and 5 g of phenol, 2.67 mmol PTSA or 1.33 mmol SA, were reacted at 140°C to 150°C (Mun et al. 2006). Because the cellulose and HWE contents in *P. radiata* bark were approximately 18 and 30 percent, respectively (Ku et al. 2007), the representative substrate mix in this work was chosen to have this ratio, i.e., 0.45 g of cellulose and 0.75 g of HWE based on reactions of 2.5 g of

*P. radiata* bark. Other mix ratio samples were 0 to 0.75 g of HWE and 0.45 g of cellulose.

Five grams of phenol and acid catalysts (1.33 mmol SA or 2.67 mmol PTSA) was added into a 50-mL round-bottom flask that was then immersed in an oil bath (PEG #400) preheated to a given liquefaction temperature. When the liquefaction chemicals dissolved, 0.45 g of cellulose and 0 to 0.75 g of HWE were added into the flask and the starting time of liquefaction began. When the liquefaction reaction was ended, the resulting reaction mixture was cooled and diluted with 70 mL of the dioxane-water mixture (80/20, vol/vol), and the insoluble residues (liquefaction residues) were separated by filtration with a 1G4 glass filter. The residues were dried in a convection oven overnight at 105°C. Liquefaction yields were calculated as follows:

$$\begin{aligned} \text{Liquefaction yield (\%)} \\ = [1 - (\text{weight of residues/initial} \\ \text{weight of cellulose} + \text{ptHWE})] \times 100 \end{aligned}$$

Most of the liquefaction yields presented in this article were calculated using the above equation, but the liquefaction yields in Figure 1 were based on cellulose only.

The liquefaction products in dioxane-water filtrates, and the liquefaction residues, were analyzed further for combined phenol content, cellulose content, and acid-soluble and acid-insoluble polyphenol contents as described in the next sections. It is noted that the same phenol liquefaction reactions and same analytical procedures were carried out for raw *P. radiata* bark in our previous work (Mun et al. 2006), and part of the results were incorporated into the results of the present work to obtain a more complete comparison.

### Analysis procedures of dioxane-water filtrates and liquefaction residues

*Determination of the combined phenol.*—The liquefaction product in the dioxane-water solution obtained above was diluted again with dioxane solution (80/20, vol/vol) to 250 mL in a volumetric flask, and the free phenol content in the solution was analyzed by a gas chromatograph (GC-

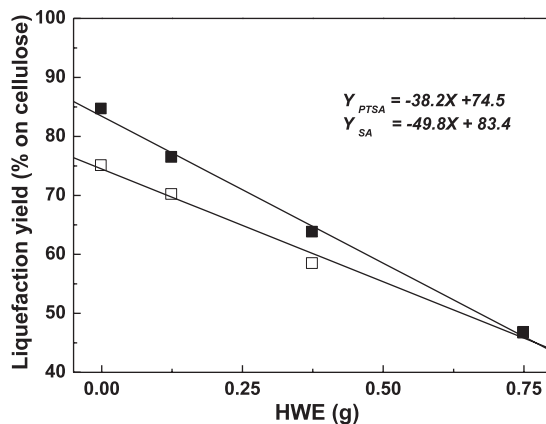


Figure 1.—Influence of hot-water extract (HWE) on phenol liquefaction of cellulose in the presence of sulfuric acid (SA; ■) and *p*-toluene sulfonic acid (PTSA; □) catalysts. Liquefaction conditions: liquefaction temperature, 140°C; liquefaction time, 20 minutes; cellulose, 0.45 g (oven dried); phenol, 5 g; SA, 1.33 mmol; PTSA, 2.67 mmol.

17A; Shimadzu, Kyoto, Japan), equipped with a flame ionization detector (FID) and CBP 20 silica-fused capillary column (25-m by 0.22-mm inside diameter [i.d.], 0.25- $\mu$ m film thickness). The oven temperature was increased from 150°C to 200°C at a rate of 5°C/min. Helium was used as a carrier gas at a flow rate of 1 mL/min. Split ratio was adjusted to 10. One microliter of solution was injected and eugenol used as an internal standard, and the total free phenol content was obtained. The combined phenol content was derived as a percentage by subtracting the free phenol content from the charged phenol (5 g).

**Determination of acid-insoluble and acid-soluble polyphenols in liquefaction residues.**—The dioxane-insoluble liquefaction residues (100 mg) from the liquefaction reactions described above were treated with 1.5 mL of 72 percent SA at room temperature for 4 hours by stirring once every 30 minutes and then the mixture was diluted to 3 percent SA by adding 55 mL of DI water. The diluted solution was further hydrolyzed in an autoclave (JS-AC60; Johnsam, Buchun, Kyungkido, South Korea) at 120°C for 1 hour. The hydrolyzate was filtered through a 0.45- $\mu$ m-pore-size membrane, and the acid-insoluble residues were vacuum dried overnight and weighed. These acid-insoluble residues were defined as the acid-insoluble polyphenols in percentages:

$$\text{Acid-insoluble polyphenols (\%)} \\ = (\text{weight of residues after acid hydrolysis/weight} \\ \text{of residues before acid hydrolysis}) \times 100$$

The acid-soluble polyphenols were then determined first by diluting the hydrolyzate removed of the acid-insoluble polyphenols to 100 mL with DI water and then analyzing the solution for polyphenol contents using an UV/Vis spectrophotometer (8452A; Hewlett-Packard, Palo Alto, California) at 290-nm wavelength. The content of polyphenols in the solution was calculated from the standard curve obtained from the various concentrations of HWE at 290 nm. The results were expressed as HWE equivalents/liquefaction residue (g).

**Determination of cellulose contents in liquefaction residues.**—The glucose content of the hydrolyzate, after determining the acid-soluble polyphenols content, was determined by first converting it to glucitol acetate in accordance with the TAPPI test method (T 249 cm-00) and then analyzing it by GC (GC-17A; Shimadzu) equipped with an FID and an SP-2380 silica-fused capillary column (30-m by 0.32-mm i.d., 0.25- $\mu$ m film thickness). The oven temperature was increased from 180°C to 250°C at a rate of 5°C/min. The injection and detection ports were set at 240°C and 260°C, respectively. Helium was used as a carrier gas with a flow rate of 2.7 mL/min. Split ratio was adjusted to 10. The amount of glucose calculated from GC analysis was then converted to the residual cellulose equivalent using the conversion factor according to the above TAPPI test method for monosaccharide to polysaccharide (0.90 for hexoses).

## Results and Discussion

### Influence of HWE on the acid-catalyzed phenol liquefaction of cellulose

To investigate the influence of the bark polyphenol components on the acid-catalyzed phenol liquefaction of the bark, HWE of bark was used as bark polyphenol substitutes.

The liquefaction reactions were carried out at 140°C for 20 minutes, which is milder than that of previous bark liquefaction reactions (Mun et al. 2006) in order to verify the influence of HWE and to analyze the liquefaction residues available from the milder reactions.

The liquefaction yields are plotted in Figure 1 against the amounts of HWE-to-cellulose ratios of samples for both SA and PTSA catalysts. The yields decreased with the increasing amounts of HWE, indicating that polyphenols seriously interfere with the acid-catalyzed phenol liquefaction of cellulose. The decreasing trend of liquefaction yields was more pronounced for SA catalyst than for PTSA catalyst; i.e., liquefaction yields for SA catalyst were more negatively affected by HWE than yields for PTSA catalyst. The colors of the liquefaction residues for SA catalyst were gradually changed from white to dark brown with increasing amounts of HWE (reddish brown by itself), but those obtained for PTSA changed from white to slightly pinkish even with the highest amount of HWE. This deep brown color of liquefaction residues observed for SA catalyst also appears to indicate that condensation reactions between cellulose and polyphenols occur more extensively with SA than for PTSA catalyst.

The effects of the polyphenol components on the phenol liquefaction of cellulose in the presence of acid catalyst were investigated further by carrying out reactions at 143°C and 150°C for 5 to 60 minutes. Because the contents of cellulose and HWE in *P. radiata* bark were reported to be about 18 and 30 percent, respectively (Ku et al. 2007), the corresponding ratio sample (0.45 g of cellulose/0.75 g of HWE) was used for liquefaction. The liquefaction yield results of these experiments shown in Figure 2 indicate that liquefaction yields rapidly increase with increasing liquefaction time for both SA and PTSA catalysts. However, the liquefaction yields increased with reaction times more markedly for PTSA catalyst than for SA catalyst, the difference becoming greater as the liquefaction time increased from 10 to 60 minutes at 143°C. The liquefaction

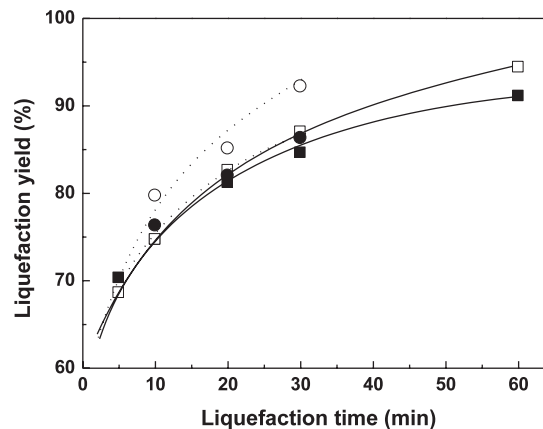


Figure 2.—Liquefaction yields as a function of liquefaction time in phenol liquefaction of cellulose and hot-water extract (HWE) mixture with different acid catalysts and liquefaction temperatures. Sulfuric acid (SA; ■) and *p*-toluene sulfonic acid (PTSA; □) at 143°C; SA (●) and PTSA (○) at 150°C. Liquefaction conditions: liquefaction temperatures, 143°C and 150°C; cellulose, 0.45 g (oven dried [o.d.]); HWE, 0.75 g (o.d.); phenol, 5 g; SA, 1.33 mmol; PTSA, 2.67 mmol. Note: Percent liquefaction yields of cellulose–HWE are based on the o.d. weight of cellulose.

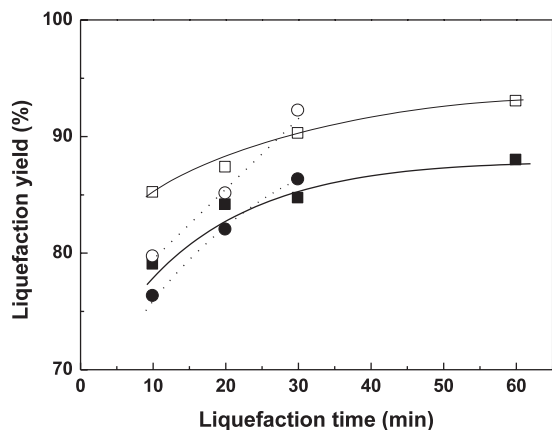


Figure 3.—Liquefaction yields as a function of reaction time in phenol liquefaction of cellulose and hot-water extract (HWE) mixture and *Pinus radiata* bark. Sulfuric acid (SA; ■) and p-toluene sulfonic acid (PTSA; □) for *P. radiata* bark; SA (●) and PTSA (○) for cellulose–HWE. Liquefaction conditions: liquefaction temperature, 150°C; cellulose, 0.45 g (oven dried [o.d.]); HWE, 0.75 g (o.d.); bark, 2.5 g (o.d.); phenol, 5 g; SA, 1.33 mmol; PTSA, 2.67 mmol. Notes: *P. radiata* bark data were taken from our previous report (Mun et al. 2006). Percent liquefaction yields of cellulose–HWE and bark are based on the o.d. weight of cellulose and bark, respectively.

yields at 150°C were all higher for PTSA than for SA catalyst at all liquefaction times. These results are comparable to those reported on the phenol liquefaction of raw bark (Mun et al. 2006), as shown in Figure 3. Overall, it is concluded that the PTSA catalyst causes fewer condensations between cellulose and polyphenols in the phenol liquefaction reactions than the SA catalyst.

### Combined phenol contents in liquefied products

Because the phenol used as liquefying solvent can react with decomposition products of cellulose (Lin et al. 2004, Mun and Jang 2009), the combined phenol content in liquefaction products provides an important index of efficiency for acid-catalyzed phenol liquefaction reactions. The combined phenol contents from liquefaction of all cellulose–HWE mixture samples and bark, determined by GC analyses shown in Figure 4, show that they increase with increasing liquefaction times for both SA and PTSA catalysts. However, at the same liquefaction times, the combined phenol contents for PTSA catalyst were always higher than those obtained for SA catalyst. The results also agreed with the results obtained with raw bark (Mun et al. 2006).

The combined phenol contents are also plotted against liquefaction yields in Figure 5 at 150°C of reaction temperature, where the two values are shown to linearly increase for both SA and PTSA catalysts. However, in the case of the bark, the combined phenol contents for SA catalyst were always 4 to 5 percent higher than those for PTSA catalyst at the same liquefaction yields. In the case of cellulose–HWE mixture samples, the combined phenol contents for SA catalyst at liquefaction yields above 83 percent were always higher than those for PTSA catalyst as well.

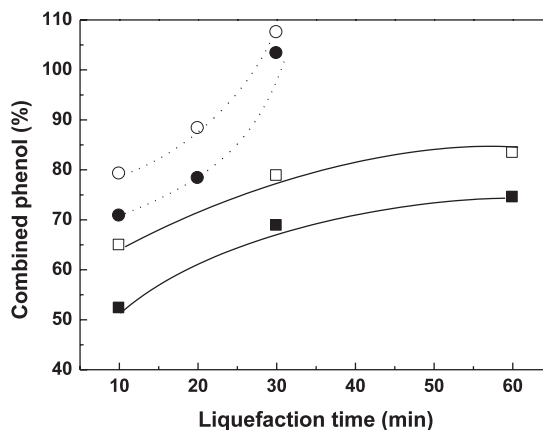


Figure 4.—Combined phenol contents as a function of liquefaction time in phenol liquefaction of cellulose and hot-water extract mixture and *Pinus radiata* bark. Liquefaction conditions and symbols are the same as in Figure 3.

The higher combined phenol contents at the same liquefaction yield were also observed at the phenol liquefaction of cellulose (Mun and Jang 2009). In the SA-catalyzed phenol liquefaction of cellulose, the combined phenol content was 50 percent higher than that for PTSA catalyst. This indicates that SA catalyst leads to a higher phenolation and liquefaction yield than PTSA catalyst during the phenol liquefaction of cellulose. However, the SA-catalyzed phenol liquefaction reaction was disturbed when the bark and cellulose with bark polyphenols were used as liquefaction substrates in spite of a higher combined phenol content than the PTSA catalyst. This result shows that phenolation is a necessary reaction in liquefaction, but an excessive phenolation during liquefaction of bark and cellulose with bark polyphenols can slow down the liquefaction reaction.

### Chemical composition of the residues from cellulose–HWE phenol liquefaction reactions

The unliquefied residues in the phenol liquefaction reactions could give useful information on the condensation reactions between cellulose and polyphenol components.

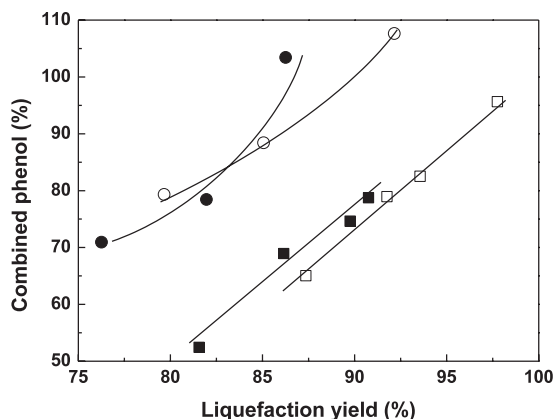


Figure 5.—Relationship between combined phenol content and liquefaction yield in phenol liquefaction of cellulose–hot-water extract mixtures and *P. radiata* bark. Liquefaction conditions and symbols are the same as in Figure 3.

**Table 1.**—Analysis results of the liquefaction residues obtained from phenol liquefaction of cellulose–hot-water extract (HWE) mixtures in the presence of p-toluene sulfonic acid (PTSA) and sulfuric acid (SA) catalysts.<sup>a</sup>

Catalyst	Liquefaction time (min)	Polyphenols content (%)			Cellulose content (%)
		Acid insoluble	Acid soluble	Total	
SA	5	5.8	2.6	8.4	36.6
	10	5.0	2.4	7.4	42.9
	30	5.8	2.6	8.4	44.5
	60	4.2	2.7	6.9	44.6
PTSA	5	4.1	1.7	5.8	40.6
	10	3.1	1.9	5.0	46.0
	30	3.6	1.9	5.5	46.8
	60	2.9	2.1	5.0	49.4

<sup>a</sup> Liquefaction conditions are the same as in Figure 6.

The residues were acid hydrolyzed to analyze cellulose and acid-soluble and acid-insoluble polyphenols. The analysis results are shown in Table 1.

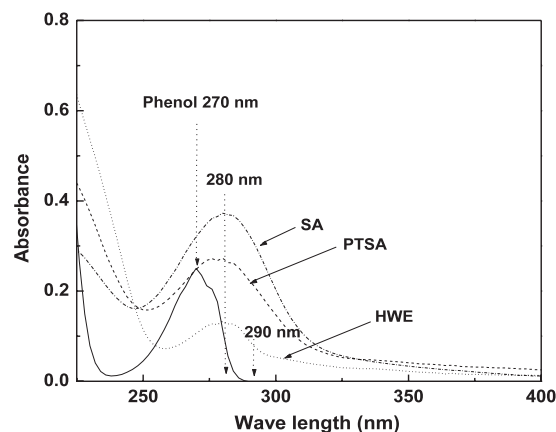
Past research indicates that most polyphenols in the bark are condensed and precipitated as acid insoluble material with lignin when lignin in the bark is determined by using 72 percent SA (Ku et al. 2007), but some of the polyphenols are expected to dissolve in the acid. The UV spectral results of HWE, phenol, and acid-soluble fraction of liquefaction residues are shown in Figure 6. Because more than 80 percent of HWE by weight is proanthocyanidins (polyphenols), HWE shows the typical UV absorption maxima at 280 nm (Ku and Mun 2007, Ku et al. 2011). The acid-soluble fractions also show similar UV spectra and absorption maxima with those of HWE, while phenol shows a slightly different maximum at 270 nm. Further, the absorption maxima difference is only 10 nm, and the phenol peak is broad and tends to reach out to 290 nm, overlapping the spectral region of the acid-soluble fractions. Therefore, the determination of the acid-soluble polyphenol contents was carried out by using the 290-nm absorption values to minimize the influence of phenol that might be produced from the combined phenol of liquefaction residues through acid hydrolysis.

The results of acid-soluble polyphenol contents obtained from this UV analysis shown in Table 1 indicate relatively constant values in the range of 2.4 to 2.7 percent for SA catalyst for all liquefaction times. In the case of PTSA catalyst, the acid-soluble contents were lower in the range of 1.7 to 2.1 percent. Furthermore, the acid-insoluble polyphenol contents also show similar trends, but they were all about three times greater than the acid-soluble polyphenol contents for both catalysts.

On the other hand, the cellulose contents in the acid-insoluble residues for PTSA catalyst were always higher than those for SA catalyst at the corresponding liquefaction times. Consequently, it is clear that polyphenol components cause retardations of acid-catalyzed phenol liquefaction reactions of cellulose–HWE mixtures because of their condensation with the cellulose components and also that PTSA catalyst reduce the condensation reactions and thus more efficiently catalyze phenol liquefaction reactions.

## Conclusions

The acid-catalyzed phenol liquefaction of cellulose was significantly retarded by the addition of polyphenols-rich



**Figure 6.**—UV spectra of phenol, hot-water extract (HWE), and the acid-soluble fractions from the acid-hydrolyzed residue of cellulose–HWE mixture phenol liquefaction in the presence of acid catalysts. Liquefaction conditions: liquefaction temperature, 143°C; cellulose, 0.45 g (oven dried [o.d.]); HWE, 0.75 g (o.d.); phenol, 5 g; sulfuric acid (SA), 1.33 mmol; p-toluene sulfonic acid (PTSA), 2.67 mmol.

HWE, especially in the presence of SA catalyst. At the similar composition of cellulose and HWE as that of *P. radiata* bark, the liquefaction results with both acid catalysts showed similar results to those of the bark liquefaction. Thus, the liquefaction yields at 150°C were all higher for PTSA than for SA catalyst at all liquefaction times as observed in the bark liquefaction. Based on the cellulose–HWE mixture phenol liquefaction results, combined phenol contents, and liquefaction residue analyses, we concluded that PTSA catalyst in the phenol liquefaction of cellulose–HWE mixtures prevents an excessive phenolation and condensation between cellulose and polyphenols in HWE and, consequently, leads to higher bark liquefaction rates than SA catalyst. More detailed study on the advantages of PTSA will be investigated in our future research.

## Acknowledgment

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (NRF-2010-013-F00006).

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