

Effect of Phenol in the Liquefaction of Pine Bark by Ethylene Carbonate-Methanesulfonic Acid*¹

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ABSTRACT

The effects of phenol during ethylene carbonate (EC) liquefaction of pine bark in the presence of methanesulfonic acid (MSA) as a catalyst were investigated. Liquefaction of pine bark using EC in the presence of acid catalyst was very difficult in comparison to wood. Mixing ethylene glycol (EG) with EC improved the liquefaction process, but the maximum liquefaction yield did not exceed 78%. Mixing 20 ~30% phenol with EC was very effective for the liquefaction and the residue was remarkably decreased. More than 95% of liquefaction was achieved when about 30% phenol was mixed with EC. The reaction conditions, such as catalyst concentration, liquefaction temperature and time, type of catalyst and liquefying agent, had a great influence on the liquefaction process. The results of the average molecular weights and the amount of combined phenols for the liquefied products indicated that sulfuric acid (SA) causes high condensation reactions compared to MSA.

Keywords: liquefaction, pine bark, ethylene carbonate, methanesulfonic acid, phenol

1. INTRODUCTION

In the last decades, intensive efforts have been devoted to the effective utilization of lignocellulosic wastes. Most of these wastes, such as sawdust, waste paper, and bark, are still burnt off or discarded into the environment causing pollution. As such, converting these wastes into useful products is a promising goal. The liquefaction of lignocellulosic wastes and other biomasses in the presence of certain organic solvents is a useful method of utilizing those biomasses efficiently. In the past few years,

many improvements have been introduced on this technique enabling the whole lignocellulosic materials to be liquefied and dissolved in many organic solvents (Yammada & Ono 1999). Phenols and polyhydric alcohols (Ono *et al.* 1996; Kurimoto *et al.* 1992; Kong and Doh 1998) are the two main liquefying agents used in the acid-catalyzed wood liquefaction. The liquefied products have many potential applications; they can be utilized in the preparation of polyurethane foams, moldings, and adhesives (Shiraishi 1989; Kato *et al.* 1990; Lin *et al.* 1995; Kong *et al.* 1999). Recently, cyclic

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carbonates alone or mixed with EG and SA as a catalyst were used successfully for rapid liquefaction of soft and hardwoods (Yammada *et al.* 2000).

Bark is produced in huge amounts by the world as waste from mechanical pulping and MDF mills. However, it has limited use in the liquefaction process because of its high lignin content and polyphenols. Mun *et al.* (1999A, B) reported that phenol and organic sulfonic acids such as MSA and *p*-toluenesulfonic acid (PTSA) are very effective for complete liquefaction of pine bark. Although phenol is a very effective liquefying agent for the bark, it has some disadvantages such as recovery costs and environmental pollution. Therefore, mixing of phenol with another solvent might decrease these disadvantages. Since EC was mentioned as a very rapid liquefying agent, it was expected that mixing EC with phenol in the presence of MSA as a catalyst would provide an effective and rapid liquefaction method for the pine bark. Liquefaction conditions (such as liquefying agent type, catalyst concentration, liquefaction temperature and time, phenol effect and catalyst type) have been investigated.

2. MATERIALS and METHODS

2.1. Materials

The pine wood (*Pinus densiflora*) and pine bark were supplied by Pan Asia Paper Korea Company and the poplar wood (*Populus alba glandulosa*) was obtained from the experimental forest of Chonbuk National University. Wood samples and bark were ground in a Wiley mill and 40~80 mesh size was used in the liquefaction.

The lignin content (Klason lignin + acid soluble lignin) for these raw materials were 21.2%, 25.7% and 48.6% for poplar, pine wood

and bark, respectively. All the chemicals used were reagent grade and obtained from commercial sources.

2.2. Liquefaction

The liquefaction experiments were carried out in a 50 ml Pyrex flask. The flask was charged with the liquefying agent and catalyst. Then, it was immersed in an oil bath connected to a temperature controller and preheated to the reaction temperature to allow complete mixing of the chemicals. Then, the flask was taken out and 2.5 g (o.d) of bark or wood meal was added to the flask. Afterwards, the flask was immersed again in the oil bath; this time being the initial reaction time. After ending the liquefaction time, the flask mixture was diluted with aqueous solution of 80% 1,4-dioxane. The diluted resultant was filtered in a G4 glass filter to separate the residue and filtrate. The residue was washed with 100% 1,4-dioxane, dried at 105°C for 12 h in an oven, and then weighed. The filtrated liquefied material was adjusted to 150 ml for molecular weight determination. The residue content is defined as a percent of the initial amount of bark or wood meal charged to the flask on a dry weight basis.

2.3. Determination of the average molecular weight

For the molecular weight determination the total filtrated liquefied material was adjusted to 150 ml with 100% dioxane, then 0.1 ml was taken from it. Dioxane and water in the liquefied materials were removed by using a rotary evaporator at 50°C. Then, the sample was diluted in 5 ml THF and filtered. The samples were analyzed with the high-performance liquid chromatograph (HPLC) using model SP 8800 ternary HPLC pump equipped with a Spectra

100 variable wavelength detector and Shodex GPC KB-802.5 column (8×300 mm). Measurements were done at 30°C, 280 nm and a flow rate of 1.0 ml/min using 100% tetrahydrofuran (THF) as the mobile phase. The molecular weights of the samples were calculated by using a calibration curve of monodisperse polystyrene standards (Mw = 114,000, 15,000, 3,600, 2,300) and a phenol (Mw = 94.11) solution. GPC graph for the liquefied material was having free phenol peak (Fig. 7). This peak was not included in the calculation of the average molecular weight.

2.4. Determination of combined phenol

For this study, the required liquefaction experiments were repeated and the total liquefied materials were adjusted to 100 ml using aqueous solution of 80% 1,4-dioxane. The amount of free phenol in dioxane-water soluble fraction was analyzed by gas chromatograph (GC) model HP 5890 Series II. GC analysis conditions were: FID detector, stainless steel column (2.1 mm × 1.8 m), silicon SE 30 (5%), flow rate 10 ml/min, carrier gas N₂, oven temperature 120°C, injection temperature 200°C and detection temperature 220°C. From the total liquefied materials, 2 ml were taken and 2 ml from the internal standard solution (eugenol) were added to them. This solution was completed to 25 ml with 100% dioxane, and then 0.2 μl from this solution was taken and injected into the GC. The amount of free phenol (FPh) was determined by using a standard phenol calibration curve.

$$FPh = [(IS_1/S)] / [C_p / (IS_2/P)] \times V$$

Where FPh is the amount of free phenol (g) in the liquefied material after liquefaction, IS₁ is the peak area of internal standard in free

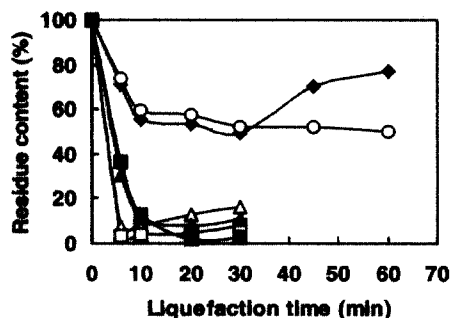


Fig. 1. Residue content as a function of liquefaction time. Raw material = 2.5 g (o.d), EC = 12.5 g, Catalyst = 3.58 mmol. ◆: Pine bark, SA, 180°C, ○: Pine bark, MSA, 180°C, △: Pine wood, SA, 180°C, ▲: Pine wood, SA, 150°C, □: Poplar wood, SA, 180°C, ■: Poplar wood, SA, 150°C.

phenol, S is the peak area of free phenol, C_p concentration of standard phenol solution used for calibration, IS₂ the peak area for internal standard in phenol used for calibration, P is the peak area of phenol solution used for calibration, V is the multiplying factor of dilution with 1,4 dioxane. The value [C_p / (IS₂/P)] was obtained from a linear equation of three standard phenol solutions used for calibration. The amount of combined phenol (CPh) which reacted with bark was determined by the following equation:

$$CPh (\%) = [(W_{Ph} FPh) / W_{bk}] \times 100$$

Where CPh is the percentage of combined phenol, W_{Ph} is the weight of total phenol used (g), FPh is the amount of free phenol (g), and W_{bk} is the oven dry weight for used pine bark (g).

3. RESULTS and DISCUSSION

3.1. EC liquefaction of bark and wood

Fig. 1 shows the dependence of the residue

content on the reaction time of EC liquefaction. In the case of pine and poplar wood, liquefaction occurred in two stages. It proceeded rapidly in the early stage, so that at 180°C, the maximum liquefaction yield was obtained after 6 min and beyond this time the residue increased slightly. Also, both wood species were rapidly liquefied at 150°C. The liquefaction yield of 63~70% was produced after 6 min and a maximum yield was obtained after 20 min.

Applying the same conditions on pine bark, in the case of SA catalyst the liquefaction occurred in three stages. In the first stage, for the first 10 min the liquefaction proceeded with a moderate rate and a residue of about 55% remained. In the second stage, the percentage of the residue decreased slowly and about 49% was remained after 30 min thereafter, the amount of the residue increased again. When the SA was replaced with MSA, the liquefaction proceeded in two stages. In the first stage, up to 10 min, the liquefaction proceeded moderately and a residue of about 59% remained. Then, the liquefaction proceeded very slowly and 50% residue was obtained after 60 min. The residue, which remained for MSA at 60 min was nearly equal to that which remained for SA at 30 min. From the above result, it can be concluded that EC was very effective for liquefaction of both soft and hardwood, but less effective for the liquefaction of bark.

3.2. Effect of EG

It was proven that lignin plays the main role in the recondensation of liquefied wood (Yao *et al.* 1993). In organosolv pulping, the hydroxyl group of alcohols reacts with lignin at its α -position preventing its condensation reactions (Nakano *et al.* 1976). Based on this fact, Yamada & Ono (1999) reported that mixing a small amount of EG (10~50%) with EC during

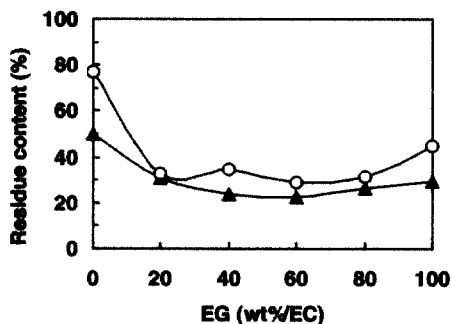


Fig. 2. Residue content as a function of EG weights of the liquefying agent. Bark = 2.5 g (o.d), Liquefying agent = 12.5 g (EC + EG), Time = 60 min, Catalyst = 3.58 mmol, Temp. = 180°C. ▲: MSA, ○: SA.

the liquefaction of softwood was very effective for lignin elution and for obtaining satisfactory liquefaction. The effect of mixing EG with EC in the liquefaction of pine bark is shown in Fig. 2. Mixing about 20~60% EG with EC was very effective, but the maximum liquefaction yield did not exceed 78%. Although the literature reported that lignin was leached out effectively when wood was treated with EG and hydrochloric acid (Yamada & Ono, 1999), the EG was not enough to leach out lignin or polyphenol in pine bark as shown in this figure. It seemed that the lignin or polyphenol in pine bark might be different in its structure and reactivity with liquefying agent in comparison with wood lignin. On the other hand, it is well known that phenol is a powerful liquefying agent, because it can react with the active sites of lignin and polyphenol and thereby prevent further condensation reactions (Mun *et al.* 1999A, B). Therefore, it is postulated that mixing phenol with EC might be very useful to obtain a high liquefaction yield.

3.3. Effect of phenol

Fig. 3 shows the effect of mixing phenol with

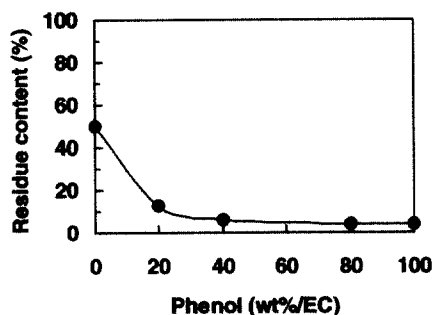


Fig. 3. Residue content as a function of phenol weight of the liquefying agent. Bark = 2.5 g (o.d), Liquefying agent = 12.5g (EC + phenol), Temp. = 180°C, Time = 60 min, MSA catalyst = 3.58 mmol.

EC in the liquefaction of pine bark at liquor ratio of 5. As shown in this figure, in the absence of phenol a residue of about 50% remained after liquefaction. Mixing 20~30% phenol with EC was very effective and the residue was remarkably decreased. More than 95% liquefaction was achieved when about 30% phenol was mixed with EC. It seems that phenol in acidic conditions could be rapidly condensed with lignin or polyphenol at an early stage in the liquefaction and this might prevent further condensation reactions. This assumption can be partly explained by the combined phenol and the molecular weight in liquefied material shown in Table 2.

Both of the efficiency and the economics of liquefaction depend on the liquor ratio. From a technical viewpoint, the use of high liquor ratio results in efficient liquefaction and gives desirable properties of liquefied material such as low viscosity. However, a high liquor ratio also increases the overall cost of liquefaction. It is therefore important to optimize the liquor ratio in order to develop an efficient and cost-effective liquefaction process. In the previous experiments, a liquor ratio of 5 was employed which produced satisfactory liquefaction results.

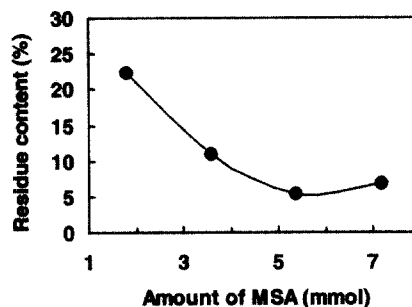


Fig. 4. Effect of MSA on the residue content. Bark = 2.5 g (o.d), Liquefying agent = 5 g EC + 2.5 g Phenol, Temp. = 180°C, Time = 60 min.

To investigate the effect of reduced liquor ratio, additional experiments were conducted using a liquor ratio of 3 and phenol/EC ratio of 1/2 (33 wt% phenol).

3.4. Effect of acid concentration

As the liquefaction of wood using an organic solvent is a solvolysis and decomposition process, the presence of a catalyst is very important for increasing the liquefaction yield. However, at a high acid concentration, recondensation reactions occur that can decrease the yield again. Accordingly, the maximum liquefaction yield cannot be obtained by increasing the catalyst concentration alone (Yao *et al.* 1993). To determine the optimum amount of catalyst, a number of experiments were carried out as shown in Fig. 4. It is already clear that with 1.79 mmol MSA, a liquefaction yield of more than 77% was obtained. Increasing the amount of MSA by 3 times up to 5.37 mmol resulted in a maximum improvement in the liquefaction process. The minimum residue content obtained at this relatively high amount of acid catalyst proved significantly the ability of MSA in retarding recondensation reactions. This advantageous phenomenon of MSA is another reason which enables high liquefaction of the bark.

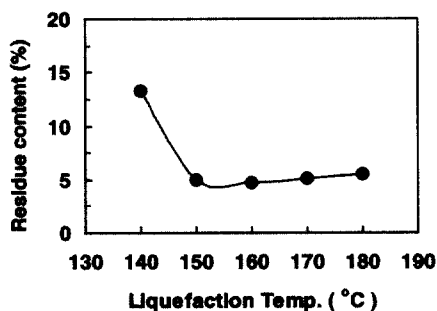


Fig. 5. Effect of liquefaction temperature on the residue content. Bark = 2.5 g (o.d), Liquefying agent = 5 g EC + 2.5 g Phenol, MSA catalyst = 5.37 mmol, Time = 60 min.

Increasing the amount of MSA more than 5.37 mmol, promoted the recondensation reactions.

3.5. Effect of temperature

Fig. 5 shows the effects of temperature on the bark liquefaction. All experiments were carried out at the EC/phenol ratio of 2/1 and 5.37 mmol of acid catalyst. From the figure it is clear that decreasing the temperature from 180°C to 150°C resulted in a negligible effect on the liquefaction yield. Generally, the residue content at all these temperatures was about 5%. This result indicates that this system was successfully used over a wide range of temperatures. In addition, the low residue obtained at 180°C means that the catalyst and the liquefying agent were both able to prevent the recondensation reactions at a high temperature. The amount of residue increased significantly as the temperature decreased to 140°C indicating that this temperature was not enough for high liquefaction. Accordingly, it was concluded that 150°C was the most suitable liquefaction temperature for this system.

3.6. Effect of time

The residue content as a function of the

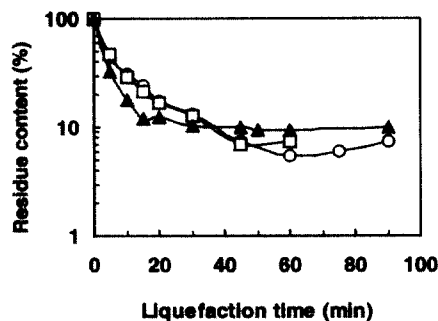


Fig. 6. Residue content as a function of liquefaction time of different catalysts. Bark = 2.5g (o.d), Liquefying agent = 5 g EC + 2.5 g Phenol, Catalyst = 5.37 mmol, Temp. = 150°C. ○: MSA, □: PTSA, ▲: SA.

liquefaction time was shown in Fig. 6. In these experiments a comparison were made between SA as a mineral acid and MSA, *p*-toluenesulfonic acid (PTSA) as organic sulfonic acids. Fig. 6 revealed that, the liquefaction of SA occurred in two stages. In the first 15 min, the liquefaction proceeded very rapidly and a residue of 12% remained. Then, a further increase in the reaction time promoted the recondensation reactions. The result was a much slower decrease in the residue content. This result means that for the SA catalyst both decomposition and recondensation reactions occurred very rapidly. As a result, a liquefaction yield of more than 91% could not be achieved. MSA and PTSA have a similar liquefaction trend. The liquefaction proceeded in three stages. In the first stage up to 10 min, the reaction proceeded rapidly but still slower than SA. In the second stage, the percentage of residue slowly decreased up to the reaction time of 45 min (yield 93%) for PTSA and 60 min (yield 95%) for MSA. Longer than these times, during the third stage, the amount of residue increased again.

Table 1. Effect of liquefying agent and catalyst type on the liquefaction yield

Liquefying agent	Catalyst type	Liquefaction yield (%)
5 g EC + 2.5 g Phenol	MSA	95.3
	PTSA	92.7
	SA	90.7
	H ₃ PO ₄	44.5
	HCl	44.2
5 g EC + 2.5 g <i>o</i> -Cresol	MSA	94.3
5 g EC + 2.5 g <i>m</i> -Cresol		95.4
5 g EC + 2.5 g <i>p</i> -Cresol		91.1
5 g EG + 2.5 g Phenol	MSA	88.9
5 g Gly + 2.5 g Phenol		89.8
5 g PEG# 400 + 2.5 g Phenol		72.0
5 g PC + 2.5 g Phenol		64.4

Temp. = 150°C, Time = 60 min, Catalyst = 5.37 mmol, Bark = 2.5 g (o.d), EC: Ethylene carbonate, PC: Propylene carbonate, EG: Ethylene glycol, PEG: Polyethylene glycol, Gly: Glycerin, MSA: Methanesulfonic acid, PTSA: *p*-toluenesulfonic acid, SA: Sulfuric acid.

Liquefaction yield (%) = 100 - [(residue (g) after liquefaction/original bark (g)) × 100].

3.7. Effect of catalyst type, phenol type and liquefying agent

Phenol liquefaction was successfully conducted by using different catalysts such as SA (Ono *et al.* 1996), HCl (Alma *et al.* 1995) and H₃PO₄ (Lin *et al.* 1994). The effects of these catalysts and organic sulfonic acids on EC/phenol liquefaction are shown in Table 1. A greater than 90% liquefaction yield was obtained when both organic sulfonic acids and SA were used as catalysts. Moreover, organic sulfonic acids gave a relatively high liquefaction yield compared with SA. This result reflects the higher capability of organic sulfonic acids to retard the recondensation reactions. In contrast, liquefaction yields for HCl and H₃PO₄ did not exceed 45%. The lower yield for HCl catalyst may be attributed to its evaporation during the liquefaction process. However, low yield was also obtained when the liquefaction process using HCl was carried out in a closed system. Therefore, another study may be carried out in

the future to determine the reason for this lower yield. The effect of different phenolic compounds on the liquefaction of pine bark was also studied. It was found that, all tested phenols gave more than a 90% yield. *m*-cresol gave the highest yield followed by phenol, whereas *p*-cresol give the lowest yield. This means that it was possible to replace phenol with other phenolic derivatives in this system. The effect of the various liquefying agents was also studied; it was found that EC/phenol system gave the highest liquefaction yield. However, replacing EC by propylene carbonate (PC) decreased the liquefaction yield by 30%. This result may be due to the permeability difference between the two organic solvents (Yammada & Ono 1999). Polyhydric alcohols such as glycerin and EG also gave satisfactory liquefaction yield (88%) but PEG#400 was not suitable for this system.

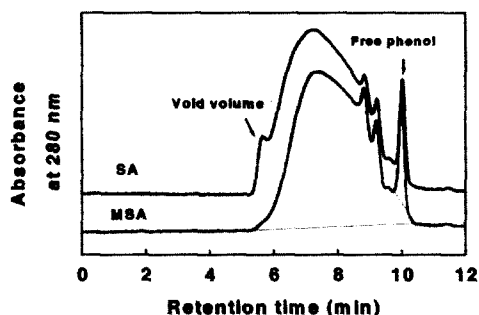


Fig. 7. GPC curve for liquefied pine bark using MSA and SA catalysts.

3.8. The molecular weight and combined phenol

Molecular weight distribution of the liquefied material depends mainly on the liquefaction conditions and the nature of the catalyst. It can give an indication on the chemical and physical properties of the liquefied products (Lin *et al.* 1997). Therefore, determining the average molecular weight (M_w) and polydispersity (M_w/M_n) for the liquefied bark under different catalysts is an important step. Fig. 7 shows GPC curve for liquefied pine bark obtained by using MSA and SA catalysts. It is clear that the graph of both catalysts have two main fractions: high molecular weight compounds (broad peak) and free phenol (sharp peak). The M_w , M_w/M_n and combined phenol (CPh) for liquefied pine bark are shown in Table 2. It is clear from Table 2 that the M_w and M_w/M_n for both MSA and SA

catalysts increased simultaneously with an increase in the liquefaction time. This result agrees with that obtained by Lin *et al.* 1997. Also, the amount of combined phenol (CPh), M_w and M_w/M_n for SA was much higher than those for MSA indicating faster liquefaction rate and condensation reactions. Under SA catalyst, the bark decomposed very rapidly resulting in many low molecular weight compounds with many reactive sites. This provided many chances for phenolation or recondensation of bark components resulting in an increase in the M_w , M_w/M_n , CPh and a decrease in the liquefaction yield. Accordingly, it can be concluded that MSA was better than SA as a catalyst because it causes less condensation and phenolation reactions.

4. CONCLUSIONS

EC/phenol mixture was used successfully for the liquefaction of pine bark. Mixing about 30% phenol with EC was very useful in preventing the action of recondensable substances in the liquefied components. Increasing the amount of MSA to 5.37 mmol led to a maximum liquefaction yield. The reaction temperature of 150°C was the minimum temperature necessary to provide a residue of less than 5%. MSA retarded the recondensation reactions for longer times compared with SA, and accordingly it gave a maximum liquefaction yield. The avera-

Table 2. Average molecular weight and combined phenol (CPh) of liquefied pine bark

Catalyst	Time (min)	Liquefaction yield (%)	M_w	M_n	M_w / M_n	CPh (%)
MSA	45	92.7	4,476	652	6.9	73.3
	60	95.0	5,376	604	8.9	75.1
	90	92.7	6,613	731	9.0	77.8
SA	45	88.9	7,477	656	11.4	83.1
	60	90.7	8,441	719	11.7	81.6

Bark = 2.5 g (o.d), Liquefying agent = 5 g EC + 2.5 g Phenol, Temp. = 150°C, Catalyst = 5.37 mmol.

ge molecular weights and the amount of combined phenol for liquefied material prepared by SA catalyst were higher than those using MSA catalyst, indicating high condensation reactions associated with SA catalyst.

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