Liquefaction of Pine Bark Using Phenol and Lower Alcohols with Methanesulfonic Acid Catalyst

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Abstract: Liquefaction of pine (Pinus densiflora) bark was conducted by using phenol/lower alcohol solvent mixtures and methanesulfonic acid (MSA) as a catalyst. A number of liquefaction variables, such as the phenol/alcohol ratio, alcohol type, water content, acid concentration, temperature and time, have been investigated to determine the optimal liquefaction conditions for pine bark. The results showed that replacing about 60% phenol with alcohols slightly increased the amount of residue. Changing the replaced alcohol from MeOH to n-BuOH increased the residue by about 12% and accordingly alcohols with short alkyl chain lengths were more effective than other alcohols. The minimum residue was obtained when the water content was about 20% and this may be due to the hydrolysis effect. Also, increasing the reaction temperature (from 160 to 190°C) and time (<90 min) significantly decreased the amount of residue. The molecular weight (Mw) determination and combined phenol (CPh) confirmed that using alcohols with short alkyl chain lengths were more effective in this system.

Keywords: Liquefaction, Pine bark, Phenol, Lower alcohols, Methanesulfonic acid

Introduction

Wood and other lignocellulosic biomass are the most naturally abundant and renewable resources in the world. The wastes of lignocellulosic biomass are still burnt off or discarded to the environment causing serious environmental problems. In the last few years, the awareness for effective utilization of these biomass wastes has increased. It has been found that liquefaction of biomass gives products with many useful potential applications such as preparation of foams, moldings and adhesives [1-3]. Phenols [4] and polyhydric alcohols [5] are the two main liquefying agents used in acid-catalyzed wood liquefaction. Recently, cyclic carbonates [6,7] have also been used successfully as a rapid liquefying agent. Among the above mentioned liquefying agents, phenol is very effective especially for lignocellulosic materials with high lignin content such as bark [8,9]. However, removal of phenol from the liquefied materials is very difficult in addition to its high recovery cost and environmental pollution. Therefore, minimizing the amount of phenol might be necessary to decrease these disadvantages. Decreasing the amount of phenol necessities decreasing the total liquid ratio. But, the liquefaction of wood is very difficult with a small liquid ratio due to the recondensation reactions [10]. As a result, it seems very difficult to reduce the amount of phenol while obtaining a high liquefaction yield. Mixing another liquefying agents with phenol may be the key to solving this problem. This way, it will be possible to reduce the amount of phenol to a minimum value without decreasing the total wood to liquid ratio. In an earlier report [11], the use of EC/phenol mixtures and organic sulfonic acids as catalyst was successfully used in the liquefaction of pine bark. However, the difficulty of recovering the liquefying agents necessitates finding another effective method. Lower alcohols are considered to be good solvents for liquefied materials in addition to their ease of recovery and lower cost. Therefore, it was expected that mixing of phenol with lower alcohols might be useful for decreasing the amount of phenol.
Experimental

Materials
Pine bark was supplied by Pan Asia Paper Korea Company (Chonju, Korea). It was ground in a Wiley mill and powder of 40 - 80 mesh size was used in the liquefaction. Lignin content (Klason lignin + acid soluble lignin) was measured as 48.6%. All chemicals used were reagent grade and obtained from commercial sources.

Liquefaction
The liquefaction experiments were carried out in a small reactor. The reactor was charged with all chemicals and 2.5 g (o.d.) of bark and then closed tightly. Afterwards, the reactor was immersed in an oil bath preheated to the reaction temperature and this time is considered to be the reaction starting time. After the liquefaction had finished, the reactor was cooled in a water bath and the liquefied materials diluted with aqueous solution of 80% 1,4-dioxane. The diluted liquefied materials were filtered in a G4 glass filter to separate the residue and filtrate. Finally, the residue was washed with 100% 1,4-dioxane, dried at 105°C for 12 h in an oven, and then weighed. The liquefaction yield was calculated as follows:

Residue content (%) = Residue (g) × 100 / Weight of raw material (o.d.)
Liquefaction yield (%) = 100 - Residue content (%)

The residue content (%) is defined as the amount of unliquefied material at the end of liquefaction.

Determination of the average molecular weight (Mw)
For the molecular weight determination the filtered liquefied material was adjusted to 150 mL with 100% dioxane, then 0.1 mL was taken from it. The dioxane and water in the liquefied material 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 high performance liquid chromatograph (HPLC) using a 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% 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 solution (Mw = 94.11). The GPC graph for the liquefied material had a free phenol peak. This peak was not included in the calculation of the total average molecular weight.

Determination of combined phenol (CPh)
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 the dioxane-water soluble fraction was analyzed by using a gas chromatograph (GC) Model HP 5890 Series II. The 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. 2 mL was taken from the total liquefied materials and 2 mL from the internal standard solution (eugenol) was added to it. This solution was adjusted 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 was determined by using standard phenol calibration curve.

\[ F_{Ph} = \frac{[ (IS_1/S) ]}{[ Cp / (IS_2/P) ]} \times V \]

where \( F_{Ph} \) is the amount of free phenol (g) in the liquefied material after liquefaction, \( IS_1 \) the peak area of the internal standard in free phenol, \( S \) the peak area of free phenol, \( Cp \) the concentration of standard phenol solution used for calibration, \( IS_2 \) the peak area for the internal standard at phenol used for calibration, \( P \) the peak area of the phenol solution used for calibration, and \( V \) the multiplying factor of dilution with 1,4 dioxane. The value \( \frac{[ Cp ]}{[ (IS_2/P) ]} \) was obtained from a linear equation of three standard phenol solutions used for calibration. The percentage of combined phenol reacted with bark was determined by the following equation:

\[ C_{Ph} = \frac{[ (W_{Ph} - FP) ]}{W_{Sa}} \times 100 \]

Where \( C_{Ph} \) is the percentage of combined phenol, \( W_{Ph} \) the weight of total phenol used (g), \( F_{Ph} \) is the amount of free phenol (g), and \( W_{Sa} \) dry weight (g) for used pine bark.

Results and Discussion

Determination of the optimum phenol/alcohol ratio
The use of phenol as liquefying agent leads to partial
cleavage of the intermolecular bonds of lignin. It also combines with lignin, especially at the α-position and accordingly prevents the condensation reactions and improves the solubility of the liquefied material [12]. Therefore, the liquefaction of pine bark, which has high lignin content, was successfully conducted by using phenol and organic sulfonic acid as a catalyst [8].

Figure 1 shows the effect of replacing phenol with alcohols (MeOH and EtOH) during the liquefaction of pine bark. As shown in the figure, it was found that the liquefaction of bark by alcohol alone in the presence of acid catalyst and water is very difficult without phenol. As a result, the residue content (%) was more than 55% at the end of the liquefaction. However, it decreased dramatically with the phenol addition and was less than 20% at 2 - 2.5 g phenol addition. Beyond this addition the residue content (%) decreased slowly. These results exhibit the fascinating ability of phenol in preventing the condensation reactions, which may have been occurred from lignin or polyphenol in bark during acid-catalyzed liquefaction, and indicate that an appropriate amount of the phenol is needed to prevent the condensation reactions during the liquefaction of bark. Thus, it can be concluded that about 2 - 2.5 g of phenol mixed with alcohol could be used successfully to give relatively high liquefaction yield. In subsequent experiments, 2.5 g of phenol was employed.

**Effect of alcohol type**

It was necessary to determine the appropriate alcohols which can be mixed with phenol to give the high liquefaction yield. As shown in Figure 2, it was found that the residue content (%) increased with increasing length of the alkyl chain of the alcohol. It increased from 11.9% in case of MeOH to 23.9% in case of n-BuOH. This result could be explained according to the solubility parameter of alcohols listed by Branup and Immergut [13] as shown in Figure 2. It is clear from the figure that the solubility parameter of alcohols decreased from MeOH to n-BuOH. This results in a decrease in the solubility of the liquefied products and accordingly increases the residue content (%). Therefore, in this study we mainly used alcohols with relatively high solubility parameters such as MeOH and EtOH for mixing with phenols.

**Effect of water**

Hydrolysis has an important role in the liquefaction of wood together with phenolysis of wood components [12]. As such, the effect of water on the alcohol/phenol liquefaction of pine bark was studied. It was found in Figure 3 that using a 5 mL solution containing 4 mL alcohol and 1 mL water decreased the residue content (%) by about 6% due to the hydrolysis effect. However, further replacing alcohol with water up to 3 mL resulted in a slight increase in the residue content (%). Replacing all alcohol with water increased the residue content (%) remarkably. The increase in the residue content (%)
could be explained according to weakening of phenolysis reactions. Accordingly, it can be concluded that, replacing 20% of a 5 mL alcohol with water improves the hydrolysis reaction without affecting the phenolysis reactions.

**Effect of acid concentration**

The presence of catalyst is very important to decrease the liquefaction temperature and time. As such, the influence of acid catalyst concentration on the residue content (%) of phenol/alcohol liquefaction was studied and the result was shown in Figure 4. The figure reveals that the residue content (%) decreased significantly with increasing the catalyst concentration from 1.79 to 3.58 mmol. It decreased from 27.3 to 11.9% for MeOH and from 34.2 to 14.8% for EtOH. Further increasing in the acid catalyst to 8.95 mmol resulted in decreasing the residue content (%) to about 8.7% for both MeOH and EtOH. But this catalyst concentration is relatively high, so we considered that the minimum acid concentration that gave a high liquefaction yield (3.58 mmol) was the optimum catalyst concentration to study the other factors.

**Effect of temperature**

Figure 5 shows the effects of reaction temperature on the residue content (%) of pine bark. It is evident from the figure that the residue content (%) for both MeOH and EtOH decreased with increasing the liquefaction temperature from 160 to 190°C. For the same catalyst, changing the type of alcohol from EtOH to MeOH resulted in a decrease in the residue content (%) by 3%-4% in the temperature range in this experiment. Similarly, for the same alcohol type, increasing the catalyst concentration from 3.58 mmol to 7.16 mmol resulted in obvious decrease in the residue content (%) at all temperatures investigated. Accordingly, it was concluded that higher temperatures accelerate the liquefaction process irrespective of the type of alcohol or the catalyst concentration.

**Effect of time**

Figure 6 presents the effects of reaction time on the residue content (%) of pine bark. It is obvious that both MeOH and EtOH have similar liquefaction trends, and the reaction proceeded in three stages. In the first stage up to 20 min, the reaction proceeded rapidly and a residue of less than 19 % was obtained for both MeOH and EtOH. In the second stage, the residue content (%) slowly decreased up to 90 min and about 10% remained. Thereafter, the residue content (%) slowly increased due to the recondensation reactions. From the above results it was concluded that the liquefaction of pine bark using alcohol/phenol mixtures occurs very fast regardless of the type of alcohol. Also, the recondensation reactions
Table 1. Average Molecular Weight and Combined Phenol (CPh) of Liquefied Pine Bark.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Catalyst (mmol)</th>
<th>Yield (%)</th>
<th>M₀</th>
<th>Mₙ</th>
<th>Mₙ/M₀</th>
<th>CPh (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>5.37</td>
<td>89.9</td>
<td>9,945</td>
<td>1,025</td>
<td>9.7</td>
<td>63.9</td>
</tr>
<tr>
<td>EtOH</td>
<td>3.58</td>
<td>85.6</td>
<td>10,736</td>
<td>708</td>
<td>15.5</td>
<td>56.9</td>
</tr>
<tr>
<td>EtOH</td>
<td>5.37</td>
<td>87.7</td>
<td>12,025</td>
<td>699</td>
<td>17.9</td>
<td>66.0</td>
</tr>
<tr>
<td>EtOH</td>
<td>7.16</td>
<td>89.2</td>
<td>12,769</td>
<td>775</td>
<td>16.5</td>
<td>68.3</td>
</tr>
</tbody>
</table>

Bark = 2.5 g (o.d), Catalyst = MSA, Liquefying agent = 7.5 g [2.5 g phenol + 4 mL alcohol + 1 mL water], Temp. = 180 C, Time = 60 min.

Figure 7. A typical GPC curve for liquefied pine bark. Note: Time = 60 min, Temp. = 180 C, MSA = 7.16 mmol, Liquefying agent = 7.5 g [2.5 g phenol + 4 mL EtOH + 1 mL water].

Molecular weight and combined phenol

The chemical and physical properties of the liquefied product can be inferred from the analysis of its molecular weight [14]. Figure 7 shows a typical GPC curve for liquefied pine bark obtained by using MSA catalyst. It is clear from the graph that the liquefied material gave a very broad curve, indicating compounds with a widely distributed molecular weight. The sharp peak at (10.1 min of RT) was assigned to the free phenol and not included in the calculation of the average molecular weight. The molecular weight (Mw), polydispersity (Mw/Mn) and combined phenol (CPh) for liquefied pine bark are shown in Table 1. It was found that at the same liquefaction conditions of 5.37 mmol catalyst MeOH gave lower Mw, Mw/Mn, CPh and higher yield compared with EtOH. This result could be explained according to the solubility parameter of alcohols. The higher solubility parameter of MeOH resulted in an increase in the solubility of the liquefied products and accordingly the yield increased. At the same time, increasing the solubility of the liquefied products decreased the recondensation reactions and accordingly decreased the Mw, Mw/Mn and CPh. Consequently, in this system it is more favorable to use an alcohol with small alkyl chain to increase the liquefaction yield and decrease the recondensation reactions. Also, it was found that increasing the acid catalyst from 3.58 to 7.16 mmol leads to an increase in the Mw, CPh and yield indicating more improvement in the liquefaction process.

Conclusions

Using 2.5 g of phenol, which was equivalent to the weight of bark, was the minimum weight that could be used successfully with alcohol to give a very low residue content (%). The alcohols with small alkyl chain lengths gave a relatively high liquefaction yield. Replacing about 20% alcohol with water improved the hydrolysis reaction. Increasing the acid concentration and reaction temperature increased the liquefaction yield. The liquefaction occurred very rapidly regardless of the type of alcohol, and the recondensation reactions appear after a long time. The molecular weight determination and combined phenol confirmed that using alcohols with short alkyl chain lengths were more effective in this system.

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References

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