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Dissolving Behavior and Fate of Cellulose in Phenol Liquefaction

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Liquefaction behavior of White Birch (Shirakamba) and cellulose with phenol were investigated using spectroscopic technique for the liquefied product and the residue. IR and NMR measurements revealed that lignin and polysaccharides were subject to degradation at the early stage of the liquefaction and their decomposed fragments reacted with phenol to produce substance bearing phenolic groups at complete liquefaction. Cellulose was found to be entirely decomposed as far as its pyranose structure was broken down. The relevant mechanism of cellulose decomposition was proposed on the basis of identified compounds from liquefied product.

Key words: Phenol liquefaction, Shirakamba, Steam-exploded lignin, Cellulose, 13C-NMR.

1. INTRODUCTION

Liquefaction of cellulosic materials is a method of converting cellolosic materials into liquid-like substance like liquefaction of coal. Many attempts have been made to gasify or to liquefy woody materials since Fierz-Davis et al. converted cellulose into gaseous product quantitatively with the aim of obtaining fuels in 1925 [1]. Simple liquefaction process has been developed mainly in Japan by using phenolic or polyhydric alcohol mediums in the presence of strong acid a decade ago [2,3,4]. This liquefaction is applicable to cellulosic wastes from wood industry and in municipal corporation. It is, therefore, of interest from the viewpoint of cellulosic waste problems if the liquefaction product could be utilized as a source of value-added materials. In order to accomplish this, it is essential to understand chemical characteristics of the products and liquefaction mechanism of wood from the viewpoint of selecting products as source for molecular designing. However, because of the diversity of wood in chemical components, there is little information on phenol liquefaction mechanism of wood and cellulose except for the investigation relevant to liquefaction using lignin model compound by Shiraishi et al [5]. Moreover, phenol liquefaction of cellulose in the presence of acidic catalyst is not clear enough. The issue whether pyranose unit from cellulose exists or not in complete liquefied product is still controversial because no convincing data has been presented. Spectral analysis should be useful to verify what occurs in the liquefaction. The objectives of this research is to elucidate the nature of phenol liquefaction in the presence of acidic catalyst and propose a possible mechanism of cellulose liquefaction by pursuing the liquefaction process with the combination of several spectral techniques and identifying some isolated componds from liquefied product of cellulose.

2. EXPERIMENTAL

Materials

White birch (Betula platyphylla) wood meal obtained from saw mill was dried in reduced pressure and used for phenol liquefaction. The moisture content was 7.4%. Three main wood components of the meal, namely lignin, α-cellulose and hemi-cellulose were measured by Klason method and Wise method [6,7]. The content was 19.9% of lignin, 53.7% of α-cellulose, and 21.6% of hemi-cellulose, which was in good agreement with literature value [8]. A dry commercial cellulose from linter pulp (100-200 mesh, Toyo Roshi Inc.) was used as cellulose model. Steam exploded lignin (SE-lignin) was obtained by the extraction from Shirakamba steam-exploded at 203oC for 10 min with dioxane. The yield of the lignin was almost 50% to the total lignin of Shirakamba. All the other chemicals used were the extra pure reagent grade in Japanese Industrial Standard and used as received.

Preparation of Phenol liquefied Product

In 100ml three necked flask equipped with stirrer, cooler and thermometer was charged 50 g of phenol and 0.98g of conc. H2SO4 at 50 °C. After mixing them well 10g of white birch meal or cellulose powder (dry weight base) was slowly added and mixed well. The content was heated to 150 °C and kept at the temperature for a fixed period. The content was neutralized with NaOH methanol/water solution and dried under reduced pressure. The dried material was then diluted with dioxane and separated to residue and dioxane soluble liquefied portion with glass thimble. The thimble was subject to Soxhlet extraction with dioxane again and with water so that Na_2SO_4 salt and liquefied product in the residue.
can be washed well. The dry weight of the residue was measured for the calculation of residue rate.
The dioxane solution in the Soxhlet boiler was recovered and combined to the filtrated liquefied portion. Liquefied product was obtained by the removal of dioxane with rotary-evaporation. Some liquefied products were subject to steam-distillation to remove unbound phenol for IR and NMR spectroscopic measurements.

FTIR Measurements (IR).

Several residues were analyzed by using Fourier transform infrared (FTIR) spectrometer. IR spectra were recorded on a Fuji FIRIS-25 Fourier transform spectrometer. Transmittance measurements were conducted using KBr pellet method.

13C-NMR Measurements.

13C-NMR spectra were recorded on a JEOL JMN-GSX 400 spectrometer at a frequency of 100 MHz using a complete decoupling technique. The measurements were conducted either in DMSO-d_6/ D_2O mixture (8/2 vol.) or in acetone-d6 at 27 °C.

Gel Permeation Chromatography (GPC).

Molecular weight distribution of liquefied products was examined at 40 °C in tetrahydrofuran (THF) as mobile phase using a Toyo soda HPLC-802 UR gel permeation chromatography equipped with two 60-cm polystyrene gel columns (TSK-GEL HG200 and H2000 in series). The chromatograms were monitored with a refractometer. The flow rate of THF was 1 ml a min.

Isolation of Main Molecular Species in Cellulose Liquefied Product

Molecular species of the phenol liquefied product were determined and with High Performance Liquid chromatography (HPLC) at 27 °C in methanol/H2O (8/2 vol) as mobile phase using a Simadzu HPLC LC-6A preparative GP equipped with a Shimpack CLC-ODS. column. The chromatogram was monitored with an ultra-violet spectro-photometric detector at 255 nm. The flow rate of the mobile phase was 2ml a min.

The main substance located at 7.32 min in the chromatogram was collected and purified with a Sanki Centrifugal Partition Chromatograph (CPC) using a mixture of chloroform, methanol and water (35/65/40 vol.) as eluent. Lower layer and upper layer of the mixture were used as stable phase and mobile phase, respectively.

3. RESULTS AND DISCUSSION

3.1. *Liquefaction behavior in the early stage of the Phenol liquefaction.*

Figure 1 shows the change of residue rate during liquefaction with phenol. The residue rate is defined as follows,

Residue Rate(%)= (Weight of Residue/ Weight of Wood Charged) x100

Since the phenol liquefaction provided almost 100% liquefied product soluble in some polar solvents like dioxane, the residue rate will be transformed into the degree of liquefaction as follows,

Degree of Liquefaction (%) = 100 - Rsidue Rate

As liquefaction proceeds, the residue rate decrease sharply up to around 25%, then slowly up to almost 0%. In order to investigate this liquefaction behavior, the residues and the products at different degree of liquefaction were pursued by FTIR, GPC and ^{13}C-NMR, respectively.

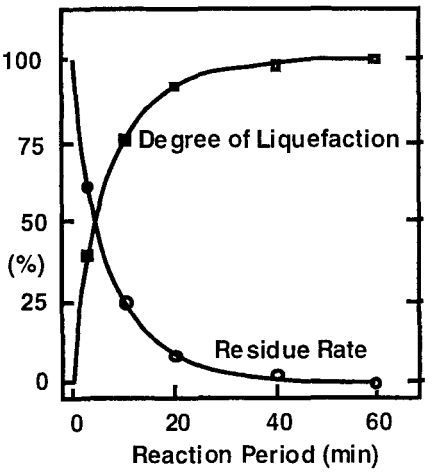

Figure 1. The residue rate and the degree of liquefaction as a function of reaction period in phenol liquefaction of Shirakamba.

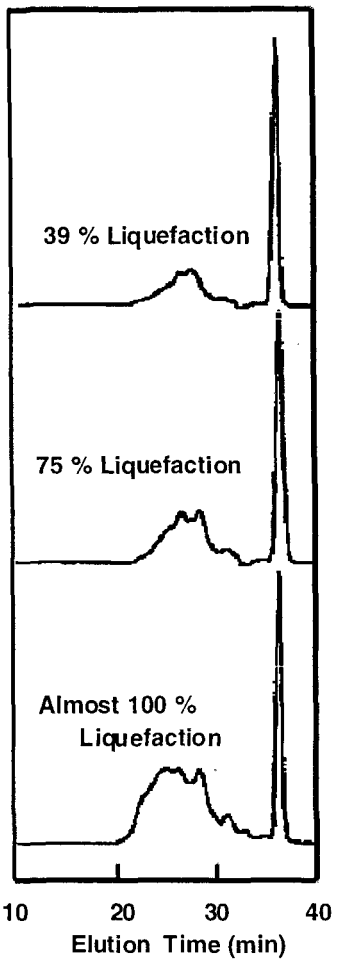

Figure 2. GPC profiles of liquefied products from Shirakamba at different liquefaction levels

Figure 2 illustrate the change of molecular weight distribution of the products during liquefaction. At 39 % liquefaction level rather low molecular weight species and unbound phenol are found whereas the distribution is broadened toward high molecular weight

side and the peak ratio of liquefied product increases as reaction proceeds.

Figure 3 represents the FTIR spectroscopic change of residues during liquefaction. The unbound phenol in the liquefied resultants was removed in order to avoid the overlaps of the peaks due to the product and unbound phenol.

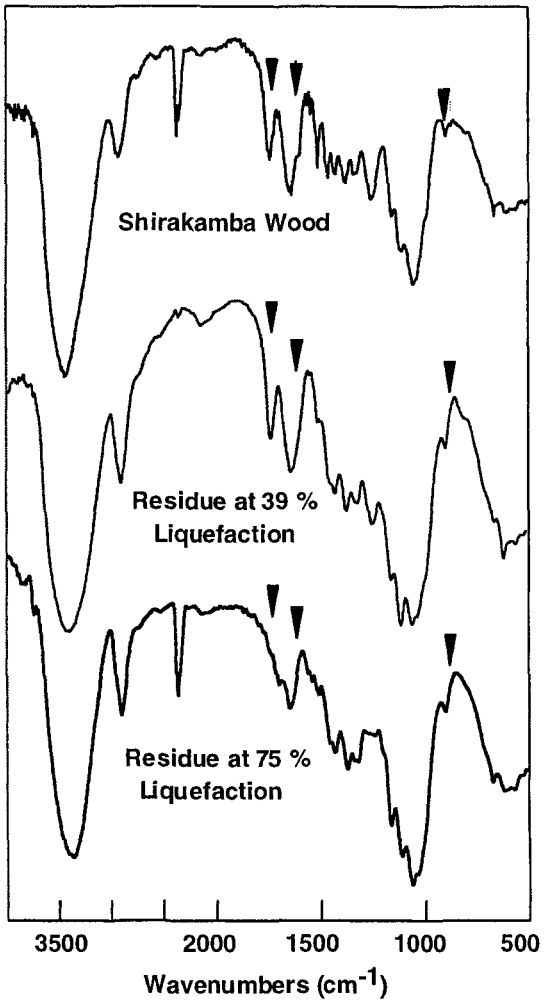

Figure 3. IR spectra of residues from Shirakamba at different liquefaction levels.

The spectra of SE-lignin, holo-cellulose and a commercial cellulose are presented as comparison in Figure 4. The spectrum of Shirakamba meal provides characteristic peaks due to lignin at 830 cm-1 (aromatic CH out of plane bending), 1510 cm-1 and 1600 cm-1 (aromatic ring bending) and those due to C-O stretching of cellulose at 985 (shoulder) cm-1, 1035 cm-1, 1058 cm-1, 1110 cm-1 and 1160 cm-1[9, 10].

As phenolation proceeds the peaks due to lignin are extinguished whereas the peaks due to cellulose is predominant. The spectrum of the residue at 75% liquefaction exhibits almost the similar spectrum to that of the commercial cellulose powder except the presence of peak at 1730 cm-1. This peak is observed in the trace of holo-cellulose. It is assigned to ester-cabonyl group of acetylic and/or uronic acid esters in hemi-cellulose [9].

These findings indicate that firstly lignin is leached out from the wood, next hemi-cellulose dissolves probably with liberating acetic group, and at last cellulose reluctantly dissolves into phenol, suggesting that the early stage of this liquefaction is much similar to the process of solvolysis pulping.

The marked difference between them exists in the last stage. Even cellulose is dissolved completely in the liquefaction.

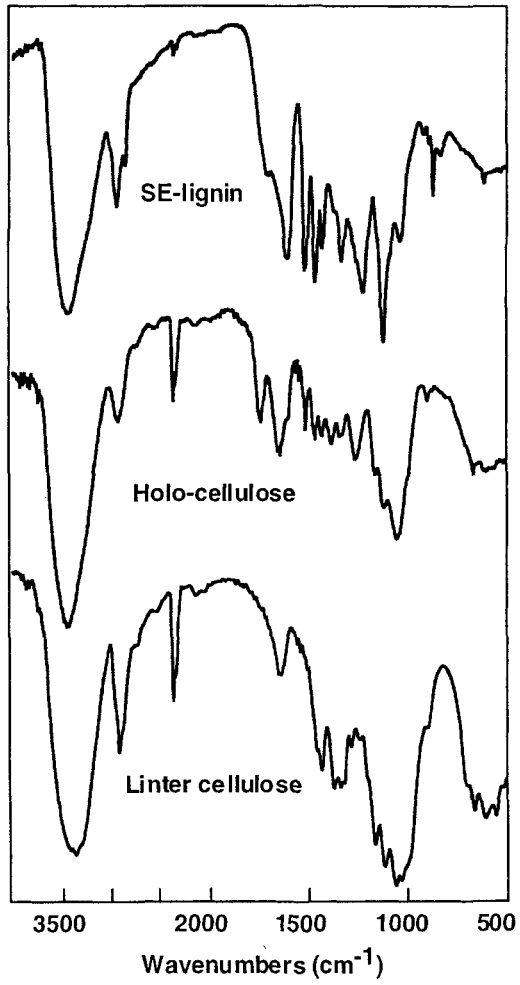

Figure 4. IR spectra of model compounds for wood.

Cellulose is known to be insoluble into common solvents since it is a poly-saccharide. The question how cellulose dissove in phenol arises.

Figure 5 shows the NMR spectrum change in the products during phenolation together with the steam exploded lignin. The main signals were assigned based on the published data [11]. The spectrum of the product at 39% liquefaction provides new signals besides the characteristic lignin signals. These new signals are attributable to bound phenol to lignin because the product mainly consists of lignin components. The distinct signals at around 156.6 ppm are assigned to the carbons attached with OH group in substituted phenols. These signals are always found in phenol liquefied products from cellulose and wood As liquefaction proceeds up to 75% liquefaction, the signals due to bound phenol are predominant whereas lignin signals are less predominant. The lignin signals due

to aromatic C-3 and C-5 carbons with C-4-OR and aliphatic carbons with β-O-4 are extinguished whereas the signals due to OMe and aromatic C-2 and C-6 in syringyl and C-3 in guaiacyl units are diminished but persistent. The same tendency has been observed in the phenolation of SE-lignin [12].

This tendency suggests that the cleavage of β-O-4 linkage and consequent addition of phenol are occurred as reported by Kratzl et al and by Yasuda et al [13,14].

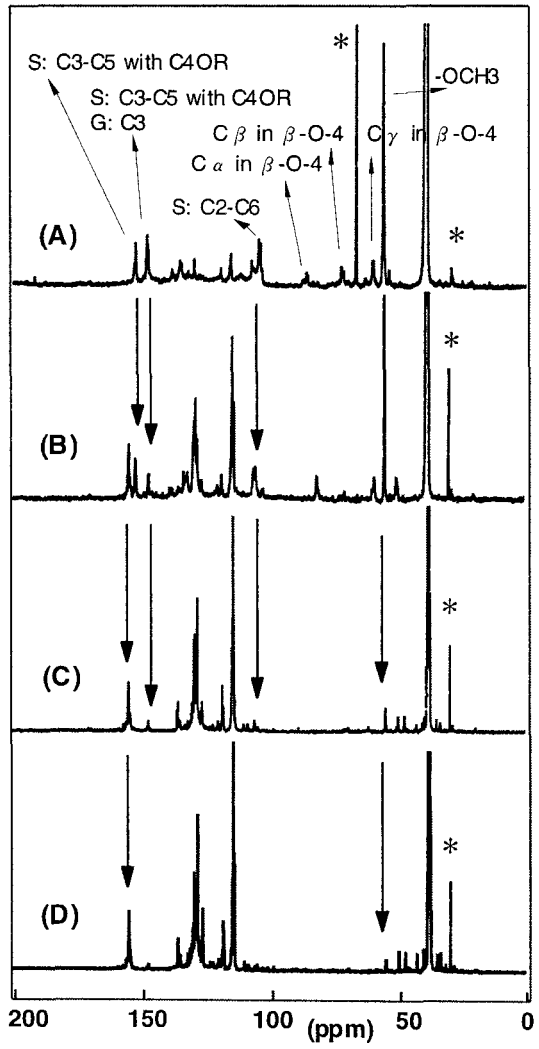

Figure 5. 13C-NMR spectra of SE-lignin (A) and liquefied products at 39% liquefaction (B), at 75% liquefaction (C), and at almost 100% liquefaction (D). Signal with asterisk is due to acetone used in treatment.

The reduction of OMe content in lignin which is reported in phenol-pulping spruce lignin by Hawkes et al is also observed, suggesting the similarity between phenol liquefaction and phenol-pulping in the early stage of the liquefaction [12]. Note that the complete liquefied product from Shirakamba gives no signals due to C-2 to C6 in pyraose ring carbon that are present in the region from 60 to 85 ppm [15]. This indicates that glucose structure of cellulose decomposes and is converted into species with no pyranose ring by phenol liquefaction. This evidence and the GPC data described above suggest that complicated reactions including condensation of decomposed fragments from lignin and cellulose with phenol would be occurred at the late stage of phenol liquefaction, to lead to complete liquefied wood.

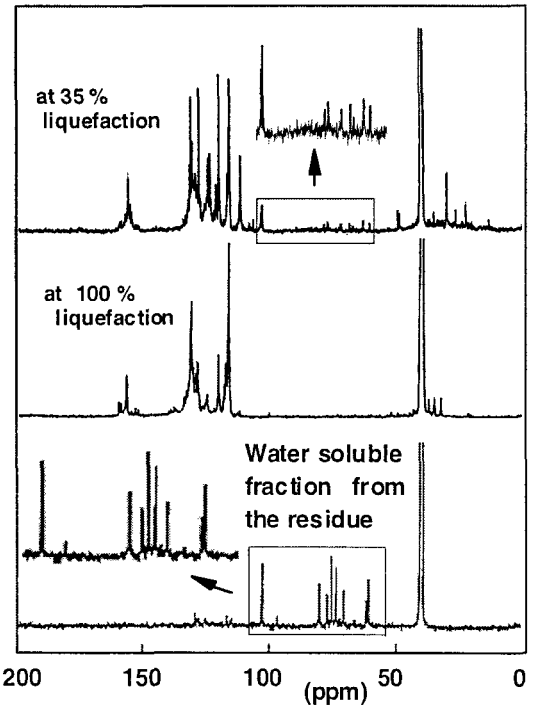

Figure 6. 13C-NMR spectra of liquefied products from cellulose at different liquefaction levels and water soluble portion in the residue at 35% liquefaction.

3.2 The fate of cellulose in phenol liquefaction

Liquefaction behavior of cellulose with phenol

Figure 6 shows the 13C-NMR spectral change of phenol liquefied product from the commercial cellulose together with the spectrum of water soluble portion in the residue at 35 % liquefaction of cellulose. Besides the strong signals due to bound phenol the residual signals due to pyranose ring are observed in the spectrum at 35% liquefaction of cellulose whereas they are extinguished at 100 % liquefaction. The water soluble portion provides the similar spectrum to that of cello-oligo-saccharides from cellulose [15].

These findings clearly demonstrate that cellulose decomposes to glucose oligo-saccharide at the early stage of liquefaction, and is then converted into substance having no pyranose ring structure in the process of phenol liquefaction.

Identified species with low molecular weight

Figure 7 illustrates the molecular weight distribution of 35% liquefied and of 100% liquefied products from cellulose together with low molecular weight substance in 35% liquefied product. The substance separated by GPC has a

molecular weight around 300. This substance was further separated into water soluble and chloroform soluble fractions. The 13C-NMR spectrum of the water soluble fraction is shown in Figure 8. The spectrum exhibits the signals due to pyranose ring carbons and substituted phenols although some extraneous signals due to methylene groups are present.

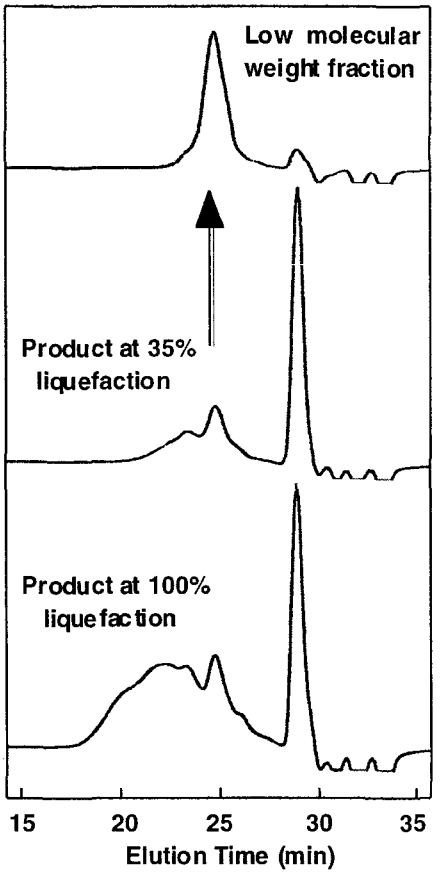

Figure 7. GPC profiles of liquefied products from cellulose at different liquefaction levels and separated low molecular weight fraction.

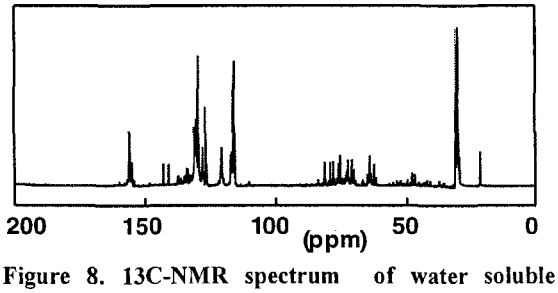

Figure 8. 13C-NMR spectrum of water soluble portion in the low molecular weight fraction shown in Figure 7.

Neither reducing end C-1 nor internal C-1 are observed. Absence of internal C-1 indicates the presence of mono-saccharide but C-1 at reducing end group is also absent. This probably suggests that the chloroform soluble portion would contain phenyl-glucosides. The production of ethylne glycol-glucosides has been proven in ethylene glycol liquefaction of celluose [16]. Attempts at purifying this fraction are in hand. These findings indicate that cellulose would be depolymerized as far as glucose via cello-oligo-saccharides, resulting into phenyl glucosides.

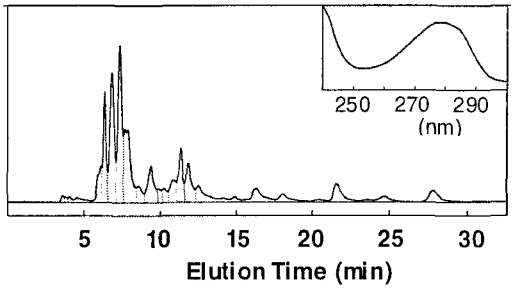

Figure 9. HPLC profile of the chloroform soluble portion extracted from the low molecular weight fraction shown in Figure 7 and the UV spectrum of the peak at 7.32 min.

Table I. 13C-NMR chemical shifts of the isolated compounds from CHCl3 soluble portion in the low molecular weight fraction shown in Figure 7.

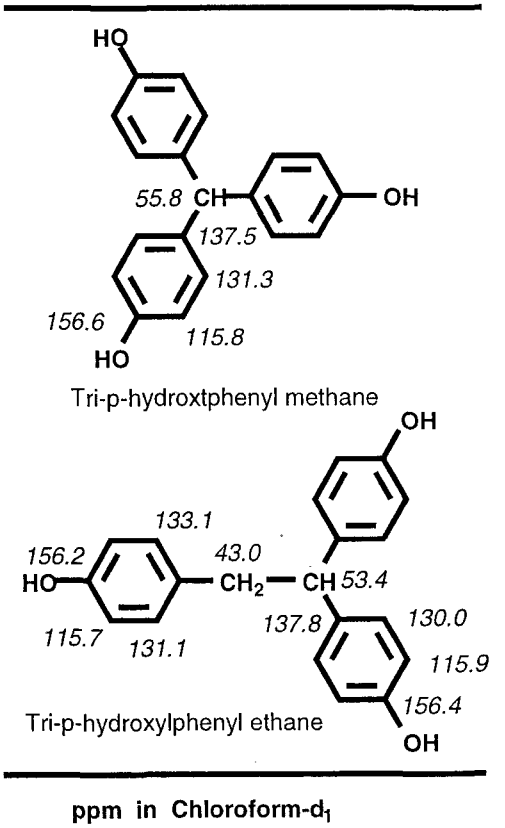

Figure 9 exhibits HPLC chromatogram of the chloroform soluble portion together with the UV spectrum of a peak at 7.32 min. elution time.

Since the fraction contains unexpectedly many species,

the fraction with strong distinct peak at 7.32 min. were collected by HPLC and purified using a CPC. Two crystalline compounds were obtained out of more than 40 species. Their assigned chemical shifts are listed in Table I .

These compounds again strongly demonstrate that pyranose ring structure is subject to degradation and decomposition first and then recombination of its decomposed fragments and phenol would occur in phenol liquefaction.

4. CONCLUSIONS

The nature of phenol liquefaction of wood is much similar to phenol solvolysis process in its early stage. The difference between them is in the behavior of cellulose. Drastic decomposition of cellulose occurs in phenol liquefaction, resulting liquefied product bearing phenolic functional groups that may help solubility in some organic solvents.

We propose the liquefaction mechanism as shown in Figure 10 representing how cellulose would dissolve in phenol in the presence of acidic catalyst.

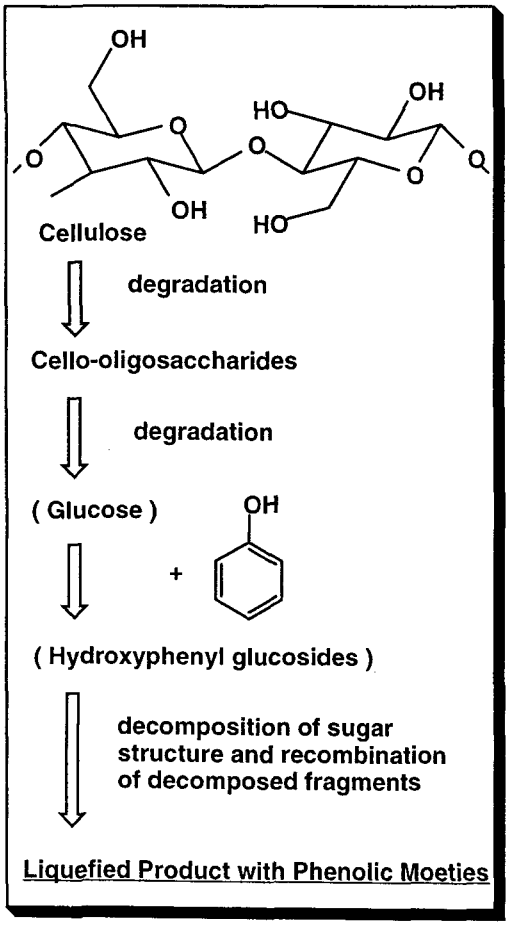

Figure 10. Proposed mechanism of phenol liquefaction of cellulose.

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