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A Refining and Structural Modification Process of Lignocellulosics at Room Temperature by Combined Hydrolysis-Phenolysis†

Masamitsu FUNAOKA, Shunsuke FUKATSU*1, Hideki SAWAI*2,
Masayuki SAGO*3, Kaori HAMAGUCHI and Junsuke MATSUE

Faculty of Bioresources, Mie University

Abstract

A new technique (swelling-solvation process) for the total utilization of lignocellulosics has been proposed. This process is due to a combination of the swelling of carbohydrates by concentrated acid and the solvation of lignin with phenol derivatives. The separation of wood into lignin and carbohydrates proceeds almost quantitatively at room temperature within 20 min, independent of species. The resulting lignin has several distinctive properties which conventional lignins do not have. For example, it is highly phenolic and scarcely has conjugated systems, showing a white color. On the other hand, the carbohydrates separated can easily be converted to monosaccharides in the same reaction system. This process would be applicable for any kind of phytomass to give perfect separation because of the decomposition of tissue structures during the treatment.

Key words: phytomass refining · lignin · carbohydrate · phenolysis · hydrolysis

Introduction

Recently, attention has been turned to the use of phytomass (lignocellulosic biomass) in the place of petroleum for chemical feedstocks. However, the phytomass refining must be done before use, since it is composed of carbohydrates and lignin which are totally different in structure and in properties.

The methods used for the phytomass refining should satisfy the following requirements:

1. The separation proceeds quickly and perfectly.
2. The separation does not cost too much.
3. The method can be used with any kind of phytomass.
4. There is no modification of the constituents to less reactive forms during the separation.

Especially, to avoid complicated modification of lignin is mandatory for the total utilization of phytomass. Furthermore, taking the present difficulty of lignin utilization into account should be developed an advanced process which not only separates lignin quantitatively but also gives lignin the improved reactivity and some

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Present address *1 Sunstar Engineering Inc.
*2 Mie Prefectural Office
*3 Honshu Paper Co., Ltd.

functions. In this standpoint, the new utilization process of phytomass by a combined hydrolysis-phenolysis (the swelling-solvation process) has been proposed[1,2].

The present paper deals with the separation behavior of wood constituents and the properties of the resulting lignins in the swelling-solvation process.

Swelling-Solvation Process

Several methods for the phytomass refining have been proposed recently[3-7]. However, most of them have been developed with the major purpose of manufacturing pulp or utilizing the carbohydrate moiety of phytomass. In conventional processes, the lignin utilization has not been taken into account at all in the developing steps of the processes and the lignin has been regarded as a barrier for the carbohydrate utilization. Consequently, the lignin is subjected to unspecifical and very complicated structural modifications during the separation and the resulting lignin does not have any distinctive structural characteristics. It would be impossible or very difficult to lead high performance products from lignins subjected to complicated structural modifications.

For the total utilization of phytomass constituents should be done approaches for the phytomass refining from angles different from conventional processes. One of them is designing the process with the primary purpose of utilizing lignin, in which carbohydrates are regarded as a barrier for the lignin utilization. That is, for the phytomass refining, lignin is not destroyed as conventional processes, but the carbohydrate barrier is destroyed to give perfect separation of carbohydrates and lignin. Phytomass utilization should not be limited to the manufacture of pulp, but that for chemical feedstocks will be important in the future. For this purpose should also be developed the process in which carbohydrates are depolymerized directly to monomers and oligomers without manufacturing pulp. Furthermore, quantitative depolymerization of carbohydrates is much easier than that of lignin, since carbohydrates have simple interunit linkages.

However, lignin is also subjected to complicated structural modifications during depolymerizing carbohydrates to get less reactive. For example, the decomposition of carbohydrate constituents in phytomass can be achieved quantitatively by concentrated acid treatment, but the behaviors of carbohydrates and lignin are totally different during the treatment. Cellulose is swollen, followed by partial hydrolysis and dissolution into the acid solution. On the other hand, lignin forms insoluble materials by self-condensation which are rigid and less reactive. Therefore, the key point to design a new process aiming at the utilization of both lignin and carbohydrates is how to avoid lignin modification to less reactive forms during the treatment.

The swelling-solvation process is a new technique for the rapid separation and structural modification of phytomass constituents aiming at their utilization. This process is due to a combination of the solvation of lignin with phenol derivatives and the swelling and dissolution of carbohydrates by concentrated acid. The process consists of the two steps (Fig. 1).

First step—Cresol treatment

A phenol derivative, for example *p*-cresol, is a good solvent for lignin, having reactivity similar to that of lignin phenyl nuclei. Furthermore, it does not mix with concentrated sulfuric acid at room temperature. Wood meals are mixed with *p*-cresol at room temperature first. *p*-Cresol has an affinity to lignin and is readily absorbed into wood to solvate with lignin.

Second step—Concentrated sulfuric acid treatment

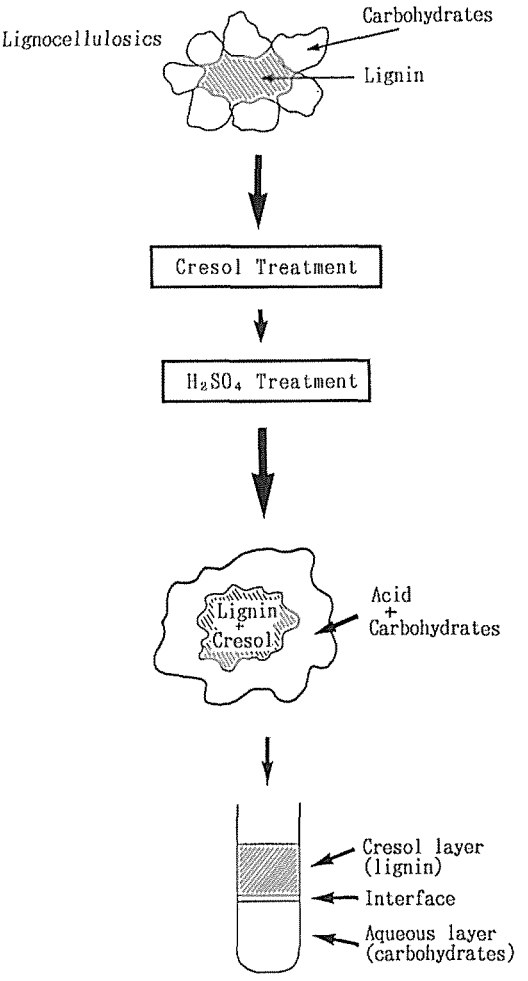

Fig. 1. Swelling-solvation process.

Seventy-two percent sulfuric acid is added to the cresol-wood mixture with vigorous stirring at room temperature. Sulfuric acid has a strong affinity with carbohydrates, resulting in the decomposition of tissue structures by swelling cellulose. During this process, lignin is always surrounded by cresol which is not mixed with sulfuric acid. As a result, the drastic attack of sulfuric acid to lignin is greatly suppressed. Lignin contacts with the acid for a short time in the interface between cresol and sulfuric acid, and the resulting carbonium ions (mainly benzyl carbonium ions) are quickly stabilized by cresol, converting lignin to highly phenolic diphenylmethane type materials. That is, the key point of this process is that carbohydrates and lignin are in the different phases during the treatment (Fig. 1).

—Separation—

By stopping the stirring after the acid treatment, the reaction mixture (a suspension) can be easily separated into cresol and aqueous layers. Lignin is contained in the cresol layer, whereas carbohydrates in the aqueous layer (Fig. 1).

Results and Discussion

Separation behavior of lignin

Treatment conditions

The yield of separated lignin showed a maximum at 20 min, after which it remained almost unchanged until 60 min (Fig. 2). On the other hand, in the case of birch, the yield of lignin reached a maximum by the treatment for 10 min.

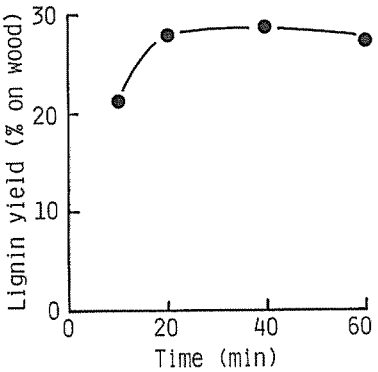

Fig. 2. Effect of treatment time on the separation of lignin.
Swelling-solvation condition:
Sample; Yezo spruce
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C

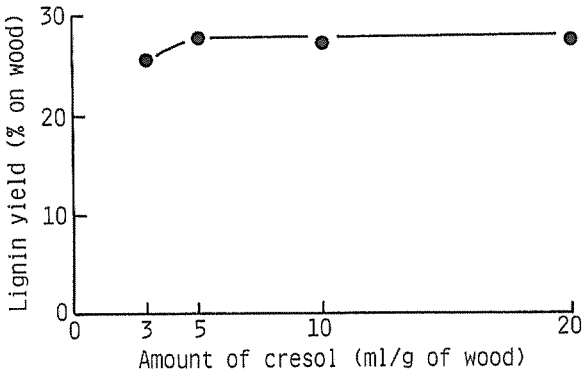

Fig. 3. Effect of cresol on the separation of lignin.
Swelling-solvation condition:
Sample; Yezo spruce
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 60 min

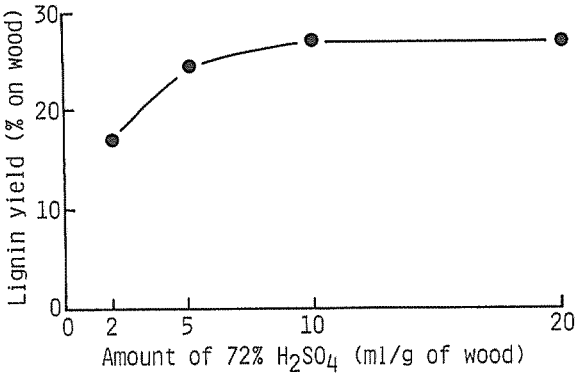

Fig. 4. Effect of sulfuric acid on the separation of lignin.
Swelling-solvation condition:
Sample; Yezo spruce
p-Cresol; 10 ml/g wood
Temp.; 25°C
Time; 60 min

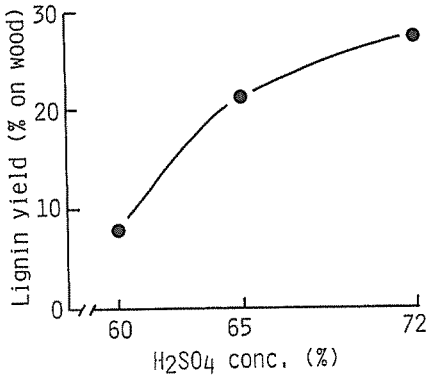

Fig. 5. Effect of sulfuric acid concentration on the separation of lignin.
Swelling-solvation condition:
Sample; Yezo spruce
p-Cresol; 10 ml/g wood
H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 60 min

The yield of lignin remained constant at more than 5 ml of cresol/g of wood (Fig. 3). However, the molecular weight of the resulting lignin was lower with the cresol amounts of 3 ml and 5 ml, indicating that the depolymerization of lignin was accelerated with a decreasing amount of cresol.

The yield of lignin increased with increasing ratio of 72% sulfuric acid from 2 ml to 10 ml, above which it remained constant (Fig. 4). However, the yields are not so different between sulfuric acid additions of 5 ml and 20 ml, showing that 72% sulfuric acid is effective for separation in small amounts. The yield of lignin from birch decreased slightly with a decreasing ratio of 72% sulfuric acid from 5 to 2. However, the degree of decrease was smaller, compared with that in spruce, and hardwood lignin was always depolymerized to a greater extent than softwood lignin.

The yield of lignin was quite low with 60% sulfuric acid, because of the insufficient swelling of carbohydrates (Fig. 5). The yield of lignin increased with 65% sulfuric acid, but the molecular weight of separated lignin was still high ($\overline{M}_w$ ca. 6000). With 72% sulfuric acid, the lignin yield increased up to about 100%, and the molecular weight of lignin decreased to $\overline{M}_w$ ca. 3000. These facts indicate that both processes—swelling of carbohydrates and depolymerization of lignin—are important for rapid separation.

Wood species

In softwoods, lignin yields got about 100% at 20 min and slightly increased at 60 min. In hardwoods, it was not so different between 20 and 60 min or slightly decreased, due to the formation of ether-soluble fractions (Table 1). This difference in the separation behavior is due to the difference not in tissue structures between softwoods and hardwoods but in lignin structures such as the distribution and quantity of ether linkages and the degree of condensation.

As obvious in Table 1, the swelling-solvation process is applicable for any wood species to give the perfect separation, because the tissue structures are destroyed by the swelling and dissolution of carbohydrates during the treatment.

Table 1. Yields of S-S lignins*

(% of klason lignin)

Species		Treatment time (min)	
		20	60
Yezo spruce	*Picea jezoensis*	99.15	108.19
Japanese fir	*Abies firma*	101.71	111.84
Slash pine	*Pinus elliottii*	105.34	116.66
Japanese hemlock	*Tsuga sieboldii*	90.85	113.06
Japanese cedar	*Cryptomeria japonica*	108.83	110.31
Japanese birch	*Betula platyphylla*	118.19	102.95
Japanese oak	*Quercus mongolica*	107.70	109.30
Apitong	*Dipterocarpus grandiflorus*	94.30	101.58
Kapur	*Dryobalanops aromatica*	97.66	93.94

* Swelling-solvation condition:
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C

Separation behavior of carbohydrates

The reaction mixture was separated into two layers after the treatment (Fig. 1). Although most parts of carbohydrates were dissolved in the aqueous layer, some parts of cellulose remained insoluble with short time treatment, being in the interface between cresol and aqueous layers. Table 2 shows the distribution of carbohydrates after the treatment. With the treatment for 20 min, more than 85% of carbohydrates were already dissolved in the acid layer. The amount of insoluble interface materials was getting less with extended treatment time, as a result of insoluble cellulose converting to soluble cellulose. The carbohydrates contaminated in the cresol layer were only in the small amount (1–2%).

Table 2. Distribution of carbohydrates in the cresol layer, the aqueous layer and the interface after swelling-solvation treatment*

Treatment time (min)	Amounts of carbohydrates (% of total carbohydrates)		
	Aqueous layer	Interface	Cresol layer
20	86.59	11.48	1.93
60	91.43	7.20	1.37
120	95.26	3.08	1.66

* Swelling-solvation condition:
Sample; Yezo spruce
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C

Properties of separated lignin

Elemental compositions of separated lignins (S-S lignins) were very similar between species in both softwoods and hardwoods (Table 3). Compared to the compositions of milled wood lignins, S-S lignins were 5% higher in carbon and 5% lower in oxygen, due to the elimination of oxygen containing functional groups (OH) and the phenolation in those places. The amounts of combined cresol were about 25% (about 0.65 mol/C_9) in softwood lignins and about 30% (about 0.9 mol/C_9) in hardwood lignins.

In general, lignins isolated under acidic conditions have brown to dark brown color. Especially, the lignins phenolated under acidic conditions show black color. However, S-S lignins were white, having slightly pinkish color, in spite of its isolation with concentrated sulfuric acid and lots of combined cresol (25–30%). This means that protolignin was not subjected to any complicated modifications except for the phenolation in the side chains, due to the solvation with cresol. Furthermore, S-S lignins were readily dissolved to various kinds of solvents such as methanol, ethanol and acetone.

Generally, the UV spectrum of lignin has a peak at 280 nm and shoulders at longer wave length. However, S-S lignin had a sharp peak only at 280 nm, having no any other peak or shoulder (Fig. 6). The ionization difference (ΔEi) spectra of S-S lignin had a sharp peak only at 300 nm showing the presence of phenolic hydroxyl groups (Fig. 7). These facts indicate that S-S lignin is highly phenolic and has almost no conjugated systems in the side chains. This is one of important characteristics of S-S lignins.

In spite of the treatment with concentrated sulfuric acid, IR spectrum of S-S lignin was very sharp, indicating no self-condensation (Fig. 8). The spectrum of S-S lignin scarcely had the absorption around 1650 cm^{-1},

Table 3. Properties of S-S lignins*

Species	Elemental composition (%)			Combined cresol		Color	Solvent
	C	H	O	%	mol/C_9		
Milled wood lignin							
Yezo spruce (*Picea jezoensis*)	61.5	5.8	32.7				
S-S lignin							
Yezo spruce (*Picea jezoensis*)	66.8	6.0	27.2	25.9	0.65		
Japanese fir (*Abies firma*)	66.5	5.8	27.7	25.0	0.62		
Slash pine (*Pinus elliottii*)	66.9	5.9	27.2	25.7	0.64	Light pink	Methanol
Japanese hemlock (*Tsuga sieboldii*)	67.5	6.1	26.4	27.8	0.69		Ethanol
Japanese cedar (*Cryptomeria japonica*)	66.2	5.9	27.9	24.8	0.62		Acetone
							Dioxane
Milled wood lignin							THF
Japanese birch (*Betula platyphylla*)	59.7	6.1	34.2				Pyridine
							DMF
S-S lignin							etc.
Japanese birch (*Betula platyphylla*)	64.3	6.0	29.7	30.9	0.90		
Japanese oak (*Quercus mongolica*)	65.0	6.1	28.9	26.0	0.81	Light pink	
Apitong (*Dipterocarpus grandiflorus*)	67.9	6.1	26.0	33.2	0.92		
Kapur (*Dryobalanops aromatica*)	65.7	6.0	28.3	30.7	0.89		

* Swelling-solvation condition:
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 60 min

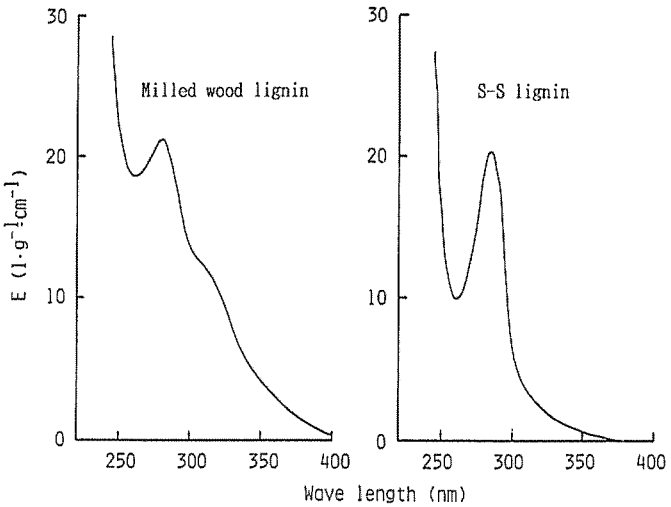

Fig. 6. UV spectra of spruce milled wood lignin and S-S lignin in methyl cellosolve.
Swelling-solvation condition:
Sample; Yezo spruce
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 20 min

assigned to conjugated carbonyl groups. Also, S-S lignin had a sharp peak around 800 cm^{-1}, due to combined cresol. These are in agreement with the characteristics of S-S lignin shown in UV spectra.

^{1}H-NMR spectrum of S-S lignin is shown in Fig. 9. The region (1.6–2.5 ppm) of acetoxyl protons in

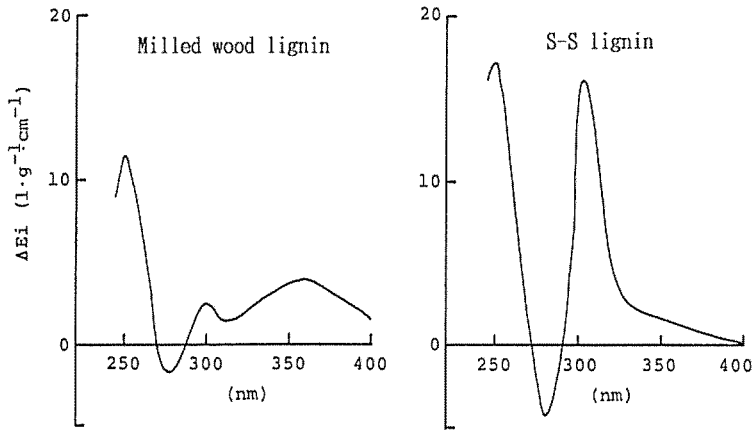

Fig. 7. Ionization difference (⊿Ei) spectra (pH 14–pH 6) of spruce milled wood lignin and S-S lignin.
Swelling-solvation condition:
Sample; Yezo spruce
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 20 min

acetylated S-S lignin is overlapped by cresolic methyl protons (2.1 ppm). However, it is obvious from the pattern that S-S lignin has lots of phenolic hydroxyl groups and still has aliphatic hydroxyl groups. The 2.50–5.20 ppm region, assigned to methoxyl and side chain protons, was broad in milled wood lignin, due to the overlap of various types of protons, whereas there were three groups of signals in addition to methoxyl signals in this region of S-S lignin. No signal was observed in the 5.75–6.25 ppm region (benzyl proton) in S-S lignin.

Table 4 shows the amounts of hydroxyl groups in S-S lignins. S-S lignins had no benzyl alcohol. Almost original amounts of Cγ-hydroxyl groups were still retained in lignin after the treatment. The quantity of phenolic hydroxyl groups is much higher in S-S lignins, compared to that of milled wood lignin, because of the cleavage of aryl ethers and the cresol combination. The quantities of phenolic hydroxyl group and combined cresol remained unchanged with extended treatment time. This implies that β-O-4 linkages were pretty stable during the treatment.

The principal modification of lignin during the swelling-solvation process would be summarized as follows: lignin is greatly protected from the attack of sulfuric acid through solvating with cresol. Lignin contacts with acid only in the interface between cresol and acid phases, and at that time, reactive benzyl alcohols and ethers mainly react with cresol. Furthermore, cresol attacks also to conjugated double bonds and carbonyl groups, resulting in no conjugated system in the side chains. There is almost no any other secondary modification. This mechanism of lignin modification was further confirmed by a treatment of milled wood lignin with swelling-solvation system[8].

Separation of phytomass into cellulose, hemicellulose and lignin

Lignocellulosics can be separated into carbohydrates and lignin within 20 min at room temperature by the swelling-solvation process. However, to achieve the total utilization of phytomass constituents, hemicellulose

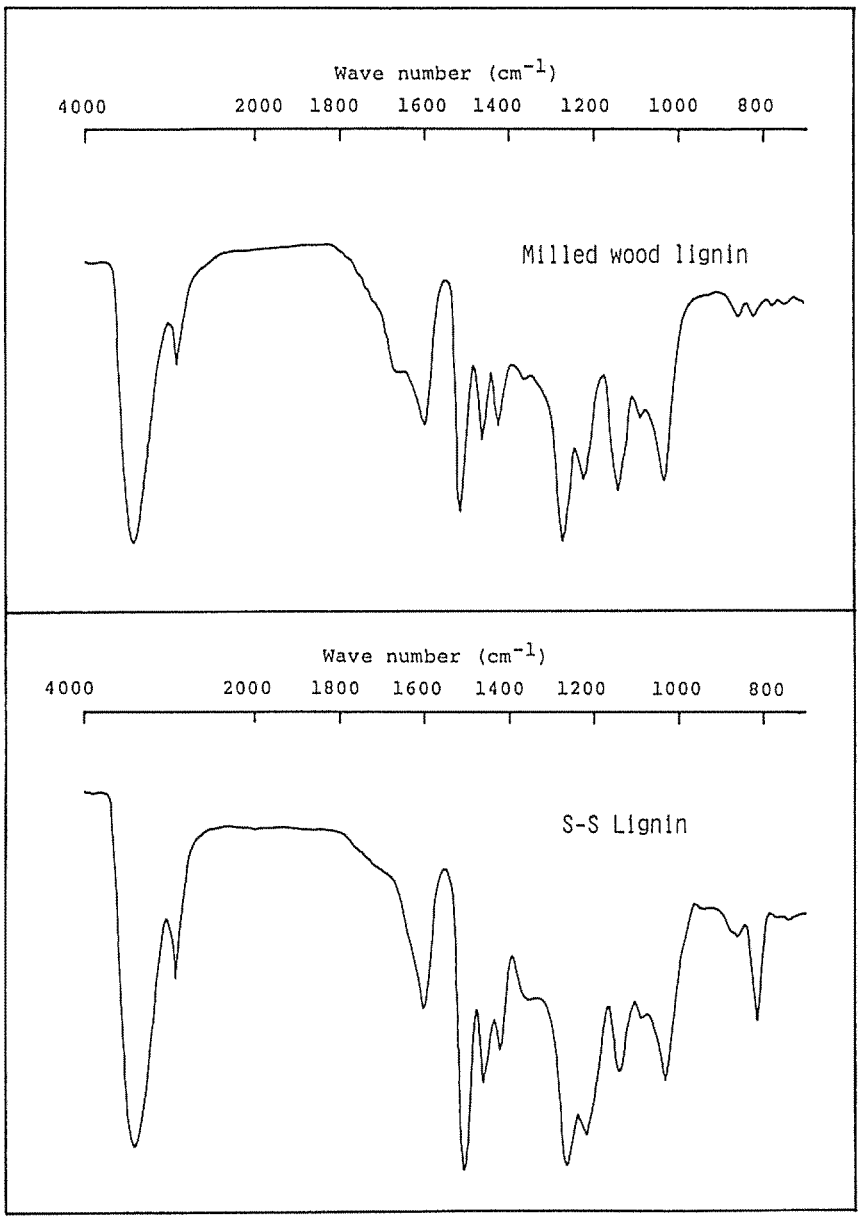

Fig. 8. IR spectra of spruce milled wood lignin and S-S lignin.
Swelling-solvation condition:
Sample; Yezo spruce
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 20 min

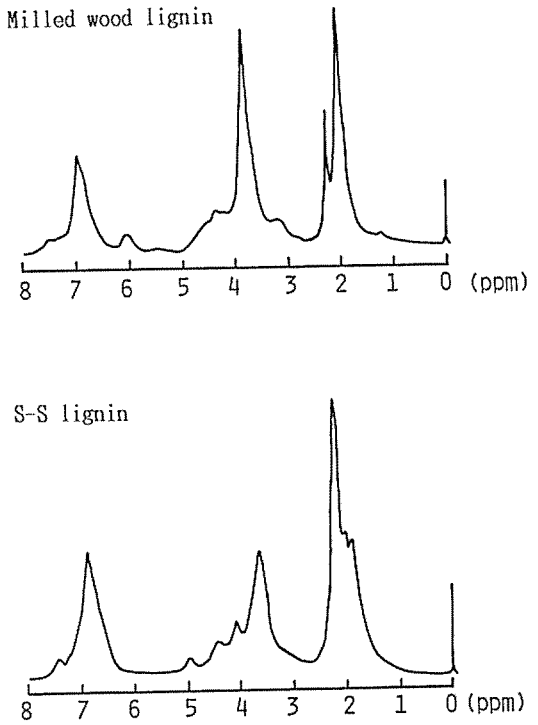

Fig. 9. ^{1}H-NMR spectra of spruce milled wood lignin and S-S lignin (acetylated).
Swelling-solvation condition:
Sample; Yezo spruce
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 20 min

Table 4. Hydroxyl group contents of S-S lignins*

Species	Hydroxyl group (mol/C_9)		
	Cα	Cγ	Phenolic
Milled wood lignin			
Yezo spruce (*Picea jezoensis*)	0.35	0.80	0.35
S-S lignin			
Yezo spruce (*Picea jezoensis*)	Trace	0.79	1.26
Japanese fir (*Abies firma*)	Trace	0.89	1.32
Slash pine (*Pinus elliottii*)	Trace	0.87	1.27
Japanese hemlock (*Tsuga sieboldii*)	Trace	0.88	1.41
Japanese cedar (*Cryptomeria japonica*)	Trace	0.86	1.31
Milled wood lignin			
Japanese birch (*Betula platyphylla*)	0.53	0.82	0.32
S-S lignin			
Japanese birch (*Betula platyphylla*)	Trace	0.80	1.51
Japanese oak (*Quercus mongolica*)	trace	0.88	1.51
Apitong (*Dipterocarpus grandiflorus*)	Trace	0.91	1.58
Kapur (*Dryobalanops aromatica*)	Trace	0.91	1.56

* Swelling-solvation condition:
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 60 min

and cellulose should further be separated, by which the following utilization of carbohydrates gets much easier. This purpose might be achieved by a mild acid hydrolysis prior to the swelling-solvation treatment (Fig. 10). For this purpose must be selected a acid hydrolysis condition in which hemicellulose is preferentially and selectively removed without complicated structural modification of lignin. There was the loss of carbohydrates corresponding to the amount of hemicellulose by the treatments with 0.5% sulfuric acid (135°C) and 30% hydrochloric acid (30°C) (Fig. 11). These acid-pretreated woods were furthermore subjected to the swelling-solvation treatment. Lignins were separated in high yield from these acid-pretreated woods (Table 5). Especially, the lignin separation from 0.5% sulfuric acid-pretreated wood was almost perfect. Of course, S-S lignins from acid-pretreated woods have slightly less amount of combined cresol, aliphatic and phenolic hydroxyl groups, due to the structural modifications during the acid treatments, compared to that from original wood (Table 5). However, distinctive characteristics of S-S lignins such as light color, high solubility and highly phenolic nature are still retained.

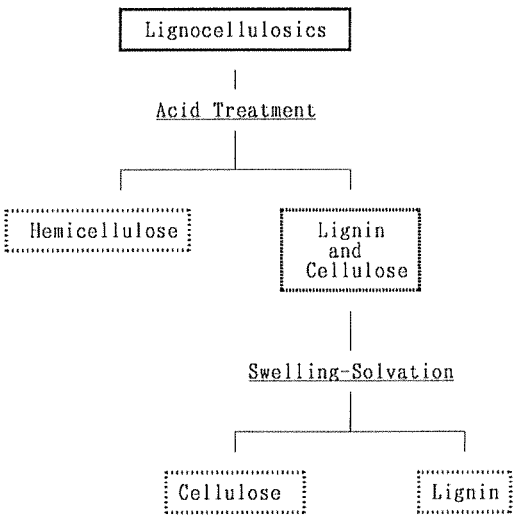

Fig. 10. Separation of phytomass constituents by a mild acid hydrolysis followed by swelling-solvation treatment.

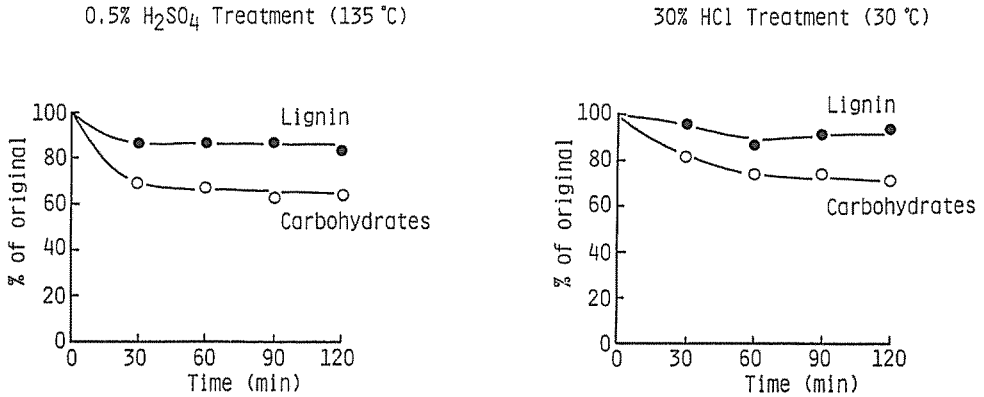

Fig. 11. Yields of lignin and carbohydrates in the acid treatments of spruce wood meal. Wood-liquor ratio, 1:10

Table 5. Yields and properties of S-S lignins* from acid-pretreated spruce woods

Pretreatment condition			Total yield (% of KL)	Cresol free yield (% of KL)	Combined cresol (mol/C_9)	Hydroxyl group (mol/C_9)	
Acid	Temp. (°C)	Time (min)				Aliphatic	Phenolic
0.5%H_2SO_4	135	60	127.60	98.29	0.56	0.64	1.13
30%HCl	30	60	116.23	89.02	0.57	0.66	1.01

* Swelling-solvation condition:
p-Cresol; 10 ml/g wood
72% H_2SO_4; 20 ml/g wood
Temp.; 25°C
Time; 60 min

Concluding Remarks

The swelling-solvation process is a new technique for the refining and structural modification of lignocellulosics by a combination of the hydrolysis of carbohydrates and the phenolysis of lignin. The key point of this process is to destroy tissue structures by the swelling and dissolution of carbohydrates with concentrated acid under the solvation of lignin with cresol.

The characteristics of the process are as follows:

1. Rapid separation.
2. No special chemicals and equipments.
3. No selectivity for wood species.
4. High reactivity and new function of the resulting lignin.

The quantitative separation of wood into lignin and carbohydrates is achieved within 20 min at room temperature. There is no need for special equipments and high heat energy because the separation proceeds at room temperature under normal pressure. The chemicals required are only sulfuric acid and cresol which are cheap. This process can be performed without large modification of conventional concentrated acid hydrolysis process, of which the technology has already been established. Furthermore, this process would be applicable for any kind of phytomass to give perfect separation because of the decomposition of tissue structures during the treatment. The resulting lignins have various distinctive characteristics that conventional lignins do not have, such as no conjugated system, high phenolic nature, high solubility, no self-condensation, white color etc. This lignin can be converted directly to various kinds of products without further modification.

The reaction system in swelling-solvation process is also effective for phenol modification of technical lignins to give lighter-colored and highly phenolic functional lignophenol derivatives[9-11]. Furthermore, this process becomes a powerful tool for estimating structures and reactivity of lignin by a combination with the nucleus exchange technique[10,12,13].

Experimental

General separation procedure

p-Cresol (10 ml) was added to wood meals (1 g) with stirring and tapping with a glass rod. After 10 min, 72% sulfuric acid (20 ml) was added to the mixture and the vigorous stirring was continued for prescribed time. By stopping the stirring, the reaction mixture was rapidly separated into cresol and aqueous layers. The cresol

layer was taken up and added dropwise to an excess amount of ethyl ether with vigorous stirring. The precipitates were dissolved in acetone, and insoluble materials (mainly contaminated carbohydrates) were removed by centrifugation. The acetone solution was concentrated under reduced pressure and added dropwise to an excess amount of ethyl ether with stirring. The precipitated lignin (S-S lignin) was collected by centrifuging and dried over P_2O_5 after evaporating the solvent.

The amounts of carbohydrates included in the cresol layer and the interface (Fig. 1) were determined by acid hydrolysis of the acetone insoluble fraction and the interface material, respectively, and that in the aqueous layer by difference.

Lignin characterization

Elemental analysis, methoxyl content, UV, IR, NMR, and GPC were used to characterize S-S lignins. Gel permeation chromatograms of lignins were determined on a JASCO TRIROTOR instrument with two shodex columns (KF802 and KF804) and UV detector (280 nm). Tetrahydrofuran was used as the eluent. Infrared (KBr disks) and ultraviolet spectra were determined on a JASCO model IR-G spectrophotometer and JASCO UVIDEC 505 spectrophotometer, respectively. ^{1}H-NMR spectra were recorded on HITACHI R-90 spectrometer (90 MHz). The solutions of lignins in $CDCl_3$ containing TMS as the internal reference were used. The amount of cresol combined with lignin was calculated based on the signal intensity of cresolic methyl protons on a ^{1}H-NMR spectrum of S-S lignin.

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加水分解およびフェノリシスを併用するリグノセルロース系バイオマス成分の分離および構造変換プロセス

船岡　正光・深津　俊輔[*1]・澤井　秀樹[*2]・左合　昌行[*3]
浜口　佳織・松江　淳介
三重大学生物資源学部
現所属　[*1]サンスター技研㈱
[*2]三重県庁
[*3]本州製紙㈱

リグノセルロース系バイオマス成分の完全分離と構造変換のための新しいプロセス（膨潤—溶媒和プロセス）を提案した。本手法はフェノール誘導体によるリグニンの溶媒和と濃酸による炭水化物の膨潤・溶解のコンビネーションに基づいており，リグノセルロース系複合体のリグニンおよび炭水化物への分離は室温，20分でほぼ達成される。分離過程でリグニンは高機能リグノフェノール誘導体へと変換され，一方炭水化物は，分離後同一反応系で直接モノマーへと誘導可能である。