Characterization of Kraft Lignin by ¹³C—Nuclear Magnetic Resonance Spectroscopy[*1]

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¹³C—NMR에 의한 크라프트 리그닌의 특성[*1]

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摘 要

Kraft pulp 폐액에 다량 존재하는 lignin을 회수 이용하기 위하여 폐액을 조제하고 유기용매로 추출 정제하여 각 fraction별로 ¹³C—NMR 및 IR 스펙트라로 측정분석하였다. 그 결과 Kirk방법 보다는 Mörck 방법으로 정제한 시료가 lignin의 특징적인 signal들을 많이 나타나고 있는 점과, 특히 MCS fraction은 방향핵이나 측쇄의 signal들이 잘 나타나고 있으며, KLI fraction에서는 methoxyl기와 C-β의 signal이 잘 나타나고 있는 것을 알 수 있었다.

SUMMARY

To recover much residual lignin from the black liquor of kraft pulp, the black liquor was extracted and purified with many organic solvents. Many kinds of lignins were isolated from each fraction obtained and the characteristics of these lignins investigated by ¹³C—NMR spectroscopy. If Mörck's method was compared with Kirk's method, Mörck's method was better than Kirk's method because the particular signals of each lignin occur more in the former than in the latter. Especially the ¹³C—NMR spectrum of the MCS fraction identifies with those of other researchers. The experiment that the kraft lignin from *Pinus densiflora* S. et Z. found in Korea was investigated by ¹³C—NMR spectroscopy was performed first in Korea.

I. INTRODUCTION

Lignin is an amorphous, aromatic biopolymer second in natural abundance only to cellulose. The biosphere is estimated to contain 3×10^{11} metric tons of lignin with an annual biosynthesis rate of ca 2×10^{10} t. Based on pulp and paper production statistics, about 50×10^{6} t/yr of lig-

nin is produced from wood plants at pulp mills worldwide.[15]

The discovery, in the latter part of the nineteenth century, that could serve as the raw material for preparation of cellulosic fibers resulted in the formation of the modern pulp and paper industry. This industry is, in a very real sense, a growth industry, and in the United States has operated at over 90% capacity for the past several years. Production is currently increasing at a rate of over 5% a year, nearly three times faster than the population growth. Predictions for the future reflect confidence of continued growth. However, one of the toughest problems that confronts the industry is that it still effectively utilizes only about one-half of its raw material.

The wood that is processed contains two of the most abundant naturally occurring organic polymers. Almost full use is made of the most abundant, cellulose, but the story is considerably different for the second polymer, lignin. In plants making pulp by chemical means, the only use for lignin until recent times was to burn it. Otherwise, the liquor has been disposed of as an aqueous solution into streams and waterways. Public resistance to this disposal has increased over the years, and the disposal problem is more acute than ever, particularly for sulfite process mills.

Although kraft process mills do not have the serious disposal problem associated with large scale dumping of spent liquors into waterways, their burning of lignin gives, at best, only a marginal return. The very nature of the pulping operations results in the lignin always being obtained in the form of diluted aqueous solutions. Although the lignins have relatively high calorific values(black liquor solids have a heat content of at least 6000 B.T.U. per pound despite their content of more than 40% inorganic compounds), the heat produced by the burning is only slightly greater than that necessary to evaporate the water from the spent liquor.[19]

The potential of the by-product lignins from kraft pulping operations (kraft lignins) as renewable chemical resources has long been recognized. Research through several decades into the utilization of these modified lignins has resulted in a number of products, and, because of changes in the economics of petroleum-based chemicals, research is probably accelerating. Ready availibility has caused kraft lignins also to be used widely as experimental lignins for studies of microbiological degradations.

Unfortunately, kraft lignins have often been studied with little if any purification, even without freeing them of nonlignin derived materials and low-molecular weight kraft degradation products of lignin. As a result, it is often difficult to interpret reported findings. In the present investigation, therefore, a softwood kraft lignin, isolated from a kraft black liquor, was fractionated according to solubility by successive extraction with organic solvents. The kraft lignin fractions obtained were characterized by IR and ^{13}C-NMR spectroscopy.

II. LITERATURE REVIEW

The structural heterogenity of kraft lignin has been studied by various methods in a number of investigations. In several of these studies the lignin was subjected to fractionation prior to the analysis. Wada[22] et al. fractionated kraft lignin by successive acidification of a

kraft black liquor, Lindberg[10] et al. by soxhlet extraction of kraft lignin with organic solvents and Lind and Detroit[9] by ultrafiltration of a kraft black liquor. The fractions were analysed in various ways, e.g. with respect to contents of functional groups, elemental composition and molecular weight. The results of these investigations showed that the contents of carboxy-lic acids and phenolic hydroxyl groups decreased with increasing molecular weight, while the content of methoxyl groups increased with increasing molecular weight.

Hatakeyama[6] et al. fractionated kraft lignin by successive precipitation with water from a dioxane solution. The fractions obtained were characterized with respect to thermal properties. The results showed that the glass transition temperature (Tg) increased with increasing molecular weight.

The average molecular weight (MW) or MW distribution (MWD) of lignins can be measured with gel permeation chromatography (GPC) or high pressure steric exclusion chromatography (HPSEC) (Connors,[2] Connors[3] et al., Faix[4] et al., Sarkanen[20] et al., Sarkanen[21] et al.).

HPSEC is much faster than GPC, however, the styrene/divinyl benzene HPSEC column packing used in previous studies will not tolerate polar lignin solvents or dissolved electrolytes (Belenkii and Vilenchick[1]). In addition, since these columns have a narrow range of pore sizes, at least four columns in series are required to seperate the entire MW range of lignin (Faix[5] et al., Connors[3] et al.).

The value of ^{13}C-NMR spectroscopy for structural characterization of lignins was first demonstrated by Lüdemann and Nimz [11,12,13] in an investigation of ^{13}C-NMR spectra of milled wood lignins from spruce and beech. ^{13}C-NMR spectroscopy is also a valuable tool for the direct observation of structural reaction. This was recently demonstrated by Nimz and Schiwind[18] during an investigation into the oxidation of DHP and milled wood lignins with peracetic acid. Morck et al.,[16,17] Luntquist[14] et al., and Kringstad[12] et al. investigated structural characteristics of kraft lignin by ^{13}C-NMR spectroscopy after kraft lignin was fractionated by successive extraction with organic solvents.

III. EXPERIMENT

1. Materials

(1) Sample tree

Pinus densiflora S. et Z. grown well on the experimental forests of Kangweon National University (Bukbang 1 ri, Bubangmyun, Hongcheongun, Kangweondo) was selected, cutted and used as sample. The characteristics of sample tree are shown in Table 1.

Table 1. Characteristics of sample tree.

Species	D.B.H.(cm)	Hight(m)	Age(yr.)
Pinus densiflora S. et Z	12.2	7.5	23

(2) Preperation of wood shavings

After barking and sawing of sample tree, the sample tree was made wood shavings with an electric plane. The wood shavings were dried at room temperature for several days till the moisture content of wood shavings reached to constant. The moisture content was 9.1 percent.

2. Methods

(1) Preperation of kraft cooking liquor and black liquor

NaOH and Na₂S were dissolved in water and

kraft cooking liquor was preperated as Table 2. showes. The characteristics of kraft cooking liquor are shown in Table 2..

Table 2. Characteristics of kraft cooking liquor.

AA(%)	20
Sulfidity(%)	30

After the digester was filled with wood shavings and kraft cooking liquor was poured into the digester, the digester was made airtight and slowly heated.

As Table 3. showes, the digester was heated to 170℃ for 1.5hr.. Cooking conditions are shown in Table 3, After the material was filtered with Büchner funnel, cellulose was removed and the liquor filtered was used as black liquor.

Table 3. Kraft cooking conditions.

Maximum temperature(℃)	170
Time to max. temperature(min)	90
Time at max. temperature(min)	90

(2) Preperation of sample lignins

1) Preperation of KL-I

A kraft lignin was precipitated from a kraft black liquor by the addition of dilute hydrochloric acid to pH8. The precipitate was centrifused, washed with water and dried, after which water was added to the precipitate to the volume of the original liquor. Dilute hydrochloric acid was added to the black liquor to pH2-3, so that kraft lignin was completely acidified and precipitated. The precipitate was washed with water and dried with the freezer dryer(Chem. Lab. Inc. SB4 Freezer Dryer) for a few days. The kraft lignin was used as Kraft Lignin-I (KL-I).

2) Preperation of KL-II

A kraft lignin was precipitated from a kraft black liquor by the addition of dilute sulfuric acid at 80℃ to pH9.5. The precipitate was filltered, washed with water and dried. The kraft lignin was used as Kraft Lignin-II(KL-II).

(3) Fractionation of sample lignins

1) Fractionation of KL-I

The kraft lignin, KL-I, was fractionated in a liquid-liquid extraction procedure developed earlier for isolation of milled wood lignin. Fig. 1 showes the seperate process. The lignin was thereby seperated into aqueous and organic fractions, and the organic fraction was further divided into ether-soluble and ether-insoluble.

After 5g of KL-I was dissolved in 210ml of pyridine: acetic acid: H_2O(9:1:4 v/v) solution
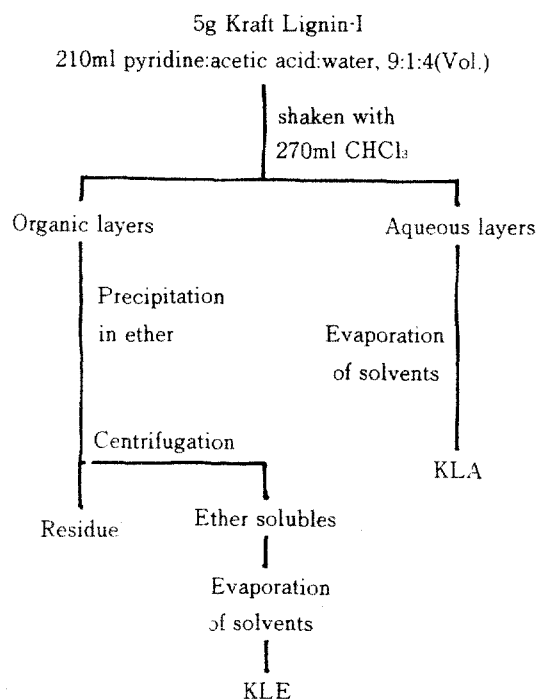

Fig. 1 Scheme of the fractionation of Kraft Lignin I

and 270ml of chloroform was poured into the solution, this solution was shakened in seperate funnel. After organic and aqueous layers were fractionated, aqueous layer was evaporated under high vaccum at 45℃ and designated KLA.

Organic layer was evaporated to ca 100ml under high vacuum, after which the concentrated solution was slowly added, with stirring, to 200ml of ehter, so that the kraft lignin was precipitated and centrifused. The solid material precipitated was designated Residue.

2) Fractionation of KL-II

The kraft lignin was fractionated according to the scheme shown in Fig. 2. A small quantity of the kraft lignin (water-extracted and dried) was used as starting material. In each extraction step the lignin was suspended in 50ml of the respective solvent (pro analysis grade) and the suspension was stirred at room temperature for 30 minutes, after which the undissolved material was filtered off and resuspended in 50ml of solvent. The suspension was again stirred at room temperature for 30 minutes. The undissolved material from this second extraction was filtered off and washed with ca 20ml of solvent. The undissolved material was carefully dried and powdered between each extraction step.
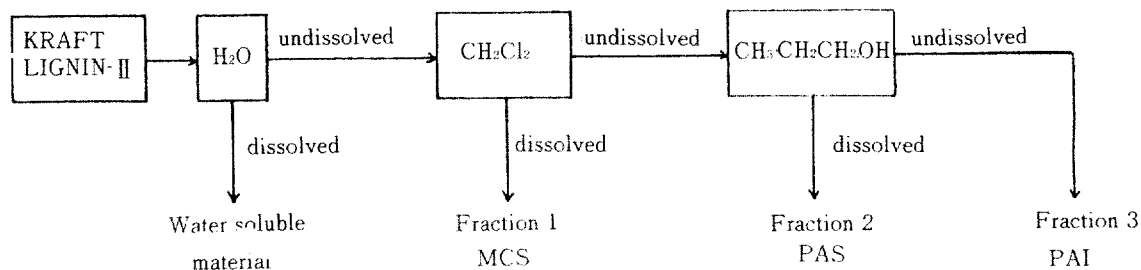
(4) Analytical instruments

The fractions obtained were investigated by IR and ^{13}C-NMR spectroscopy. IR spectra of all fractions were recorded using a PYE UICAM SP3-300 Infrared Spectrophotometer and ^{13}C-NMR spectra a Bruker AM-300 NMR Spectroscopy.

IV. RESULTS AND DISCUSSION

1. Kraft Lignin-I by Kirk's method

(1) ^{13}C-NMR spectrum of KL-I

Kraft lignin of *Pinus densiflora* S. et Z. was prepared and estracted with organic solvents according to Kirk[7]'s and Mörck's method. after which the characteristics of lignin in each fraction were investigated by IR and ^{13}C-NMR spectroscopy. As Fig. 3 is ^{13}C-NMR spectrum of KL-I from *Pinus densiflora* S. et Z., the signals caused by lignins occur well over the whole range. The assignment of each signal is shown in Table 4.. The important signals, such as the signals of guaiacyl type (129.81-147.86 ppm) related deeply to the lignin of softwood, methoxyl group (56.62 ppm) which is the important functional group, and carbonyl and carboxyl group (174.64 ppm), are well observed. In addition, many signals (14.06-50.57 ppm) of side chain are observed.

(2) ^{13}C-NMR spectrum of KLA

Fig. 2 Scheme of the fractionation of Kraft Lignin II

As Fig. 4 is ^{13}C-NMR spectrum of KLA, if KLA is compared with KL-I, the number of signals is fewer in KLA than in KL-I. It means that the amount of lignin dissolved in water is less than the amount of lignin dissolved in organic solvents. And the number of signals of aromaticring and side chain is a few.
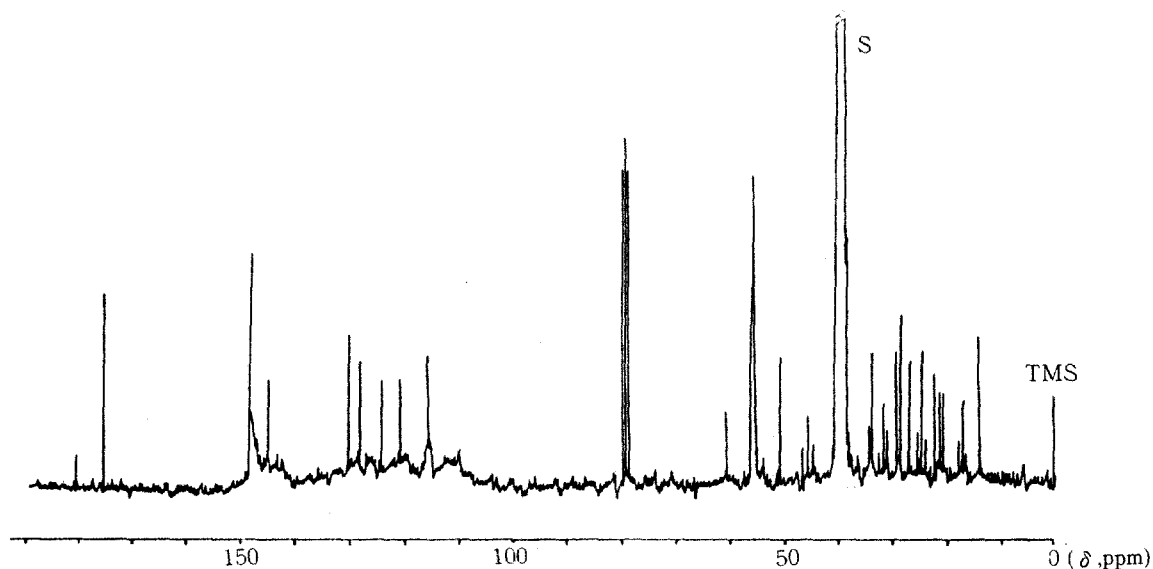

Fig. 3 ^{13}C-NMR spectrum of KL-I from *Pinus densiflora* S. et. Z. S=Solvent(DMSO-d₆)

Table 4. Assignments of signals in the ^{13}C-NMR spectrum of KL-I.
Chemical shifts are in δ ,ppm.

KLI δ ppm	Assignments(G = Guaiacyl)
180.523	C=O(aliph. COOH and/or o-quinones)
174.630	COOH(G-CHOH-COOH)
147.855	C-4G, etherified(β -aryl ethers, erythro-form)
146.538	C-4G, etherified
144.426	C-β vinyl ethers(trans-form);C-4 diaryl ethers (G4-O-G5 and G4-O-Gl types);C-4'phenylcoumaran
129.719	C-lguaiacyl(C-lG-CH=CH-)
127.812	C-5
124.325	Olefinic carbons(C-β G-CH=CH-)
120.496	C-6G-CH₂-CH₂-and G-CH-
115.337	C-5 β -aryl ethers
79.477	C-β β -aryl etehrs(threo and erythreo-forms)
60.078	γ -CH₂OH(G-CH₂-CH₂-CH₂OH; β -aryl ehters)
55.620	OCH₃
50.572	C-β phenylcoumaran and β -1 structures;C-α G-CH-G
40.054	-CH₂(C-α G-CH₂-COOH);-CH-

34.377	-CH₂(G-CH₂-CH₂-CH₂OH)
33.782	-CH₂-
31.429	-CH₂-(G-CH₂-CH₂-CH₂OH)
29.227	-CH₂-
28.984	-CH₂-(C5-CH₂-C5)
26.715	-CH₂-
24.617	-CH₂-and/or-CH₃(C-β, G-CH₂-CH₂-CH₃)
22.243	-CH₃
20.802	-CH₃, acetyl
16.933	-CH₃
14.058	-CH₃ (C-γ G-CH₂-CH₂-CH₃)

2. Kraft Lignin-II by Mörck's method

(1) ¹³C-NMR spectrum of MCS

In the case of purifying lignin from a kraft black liguor, the method is different according to researchers, and Mörck's method is better than Kirk's. As Fig. 5 is the ¹³C-NMR spectrum of MCS, MCS was obtained, extracting KL-II with methylene chloride. It is the characteristic of MCS to show many signals, such as the signals of aromatic ring (129.75-149.51 ppm), methoxyl group (55.77 ppm), and carbonyl and carboxyl group (174.76 and 179.75 ppm).

In addition, the signals of side chain (16.55-46.78 was ppm > are well obserbed.

(2) ¹³C-NMR spectrum of PAS

As Fig. 6 is the ¹³C-NMR specturm of PAS, the material not dissolved in methylene chloride was extrated with propylacohol and then the material disolved was designated PAS. The characteristics of PAS are that there is the signal of carbonyl group, that the amount of methoxyl group is more in PAS than in others, that there are the signals of C-γ or β-aryl ether, and that the signals of aromatic ring occur strongly at 129.19 and 129.47 ppm. Signals of side chain occur in the range from 10 to 40.33 ppm fewer in PAS than in MCS. The assignments of these signals are given in Table 7..
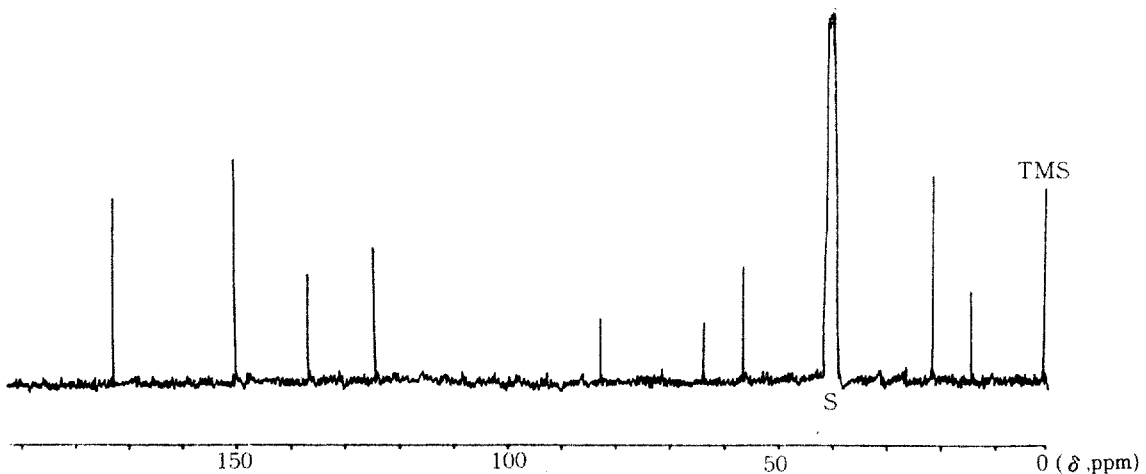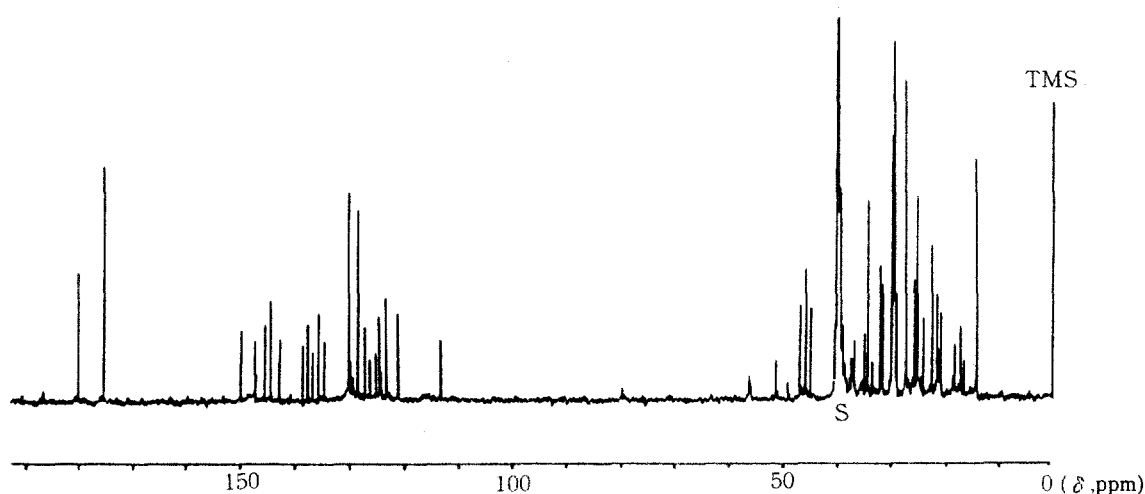

Fig. 4 ¹³C-NMR spectrum of KLA from *Pinus densiflora* S. et. Z. S=Solvent(DMSO-d₆)

Table 5. Assignments of signals in the ^{13}C-NMR spectrum of KLA.

Chemical shifts are in δ ,ppm.

KLI δ ppm	Assignments(G=Guaiacyl)
172.148	-COOH, aliphatic(G-CH$_2$-COOH)
149.647	C-5guaiacyl, etherified
136.240	C-1G-CH=CH-and G-CH(OAc)-
124.001	Olefinic carbons(C-β G-CH=CH-)
55.572	OCH$_3$
40.337	-CH$_2$-(C-α G-CG2-COOH),-CH-
21.139	-CH$_3$ acetyl
14.517	-CH$_3$

3. IR spectra of Kraft Lignin-Ⅰ

Fig. 7 is IR spectra of KL-I, and KLA. KLA was obtained, extracting KL-I with organic solvents and water. these spectra are almost similar. The skeletal vibration peaks of carbonyl group occurs at 1700cm^{-1}, the stretching vibration peak of guaiacyl type strongly at 1270cm^{-1}, and the bending vibration peak of guaiacyl type strongly at 1350cm^{-1}. In addition, in the range from 2920 to 2930cm^{-1} the stretching vibration peak of methyl or methylene

Fig. 5 ^{13}C-NMR spectrum of MCS from *Pinus densiflora* S. et. Z. S=Solvent(DMSO-d$_6$)

Table 6. Assignments of signals in the ^{13}C-NMR spectrum of MCS.

Chemical shifts are in δ ,ppm.

MCS δ ppm	Assignments(G=Guaiacyl)
179.753	C=O(aliph. COOH and/or o-quinone)
174.755	-COOH, aliphatic (G-CHOH-COOH, G-CH$_2$-CH$_2$-COOH)
149.514	C-4 guaiacyl etherified
147.032	C-4G, etherified (β-aryl ethers, erythro-form)
146.889	C-4G-CH=CH-and G-CHOH-
145.109	C-4G-CH$_2$C-3 catechol units
144.070	C-β vinyl ethers(trans-form);C-4 diaryl ethers
142.219	C-β vinyl ethers(cis-form);C-4 catechol units

138.064	C-1G-CH₂-;C-4G-CH₂-and G-CH₂-;C-4vinyl ethers
137.316	C-4G-CH₂-
136.388	C-1G-CH=CH-and G-CG(OAc)-
135.117	C-1G-CH=CH-and G-CG(OAc)-
134.329	C-1 vinyl ethers; olefinic carbons(C-α G-CH-=CH-)
129.796	C-1 guaiacyl (C-1G-CH=CH-)
129.043	Olefinic carbons(C-α p, O'-stilbenes)and C-1 guaiacyl
128.312	C-α p, P'-stilbenes(Trans-form);C-5 substituted (C-5'P, O'-stilbenes);C-2/C-6p-hydroxyphenyl units
127.893	C-5substituted(olefinic carbons)and C-1guaiacyl
126.716	Olefic carbons(C-β G-CH=CH-);C-6catechol units
124.654	C-5guaiacyl, substituted(C-5'P,O'-stilbenes)
122.823	C-5 G, acetylated;olefinic carbons
120.749	C-6guaiacyl
120.468	C-6G-CH₂-and G-CH-
55.765	OCH₃
50.865	C-β phenylcoumaran and β-1structures;C-α G-CH-G
46.784	-CH-
46.655	-CH-
44.440	-CH-
40.050	-CH₂(C-α G-CH₂-COOH);-CH-
36.785	-CH₂-
34.229	-CH₂-(G-CH₂-CH₂CH₂OH)
29.623	CH₂-(G5-CH₂-G5)
29.096	-CH₂-
27.184	-CH₂-
24.937	-CH₂-and/or-CH₃(C-β G-CH₂-CH₂-CH₃)
22.564	-CH₃
20.819	-CH₃, acetyl
16.548	-CH₃

group occurs, the stretching vibration peak of hydroxyl group around 3400cm⁻¹, and the weak twisting vibration peak of aromatic ring at 815cm⁻¹. The characteristics of them are that the absorption peaks of carbonyl group, and methyl or methylene group occur strongly in KL-I

4. IR spectra of Kraft Lignin-II

Fig.8 is IR spectra of MCS, and PAS. These fractions were obtained, extracting KL-II with organic solvents. If both spectra are compared

these spectra have similar peaks. Because many kinds of peaks occur well in MCS, it is sure that methylene chloride is a good solvent which dissolves lignin. The characteristics of MCS are that the stretching vibration peak of carbonyl group occurs very strongly at 1680cm⁻¹, that the stretching vibration peak of guaiacyl type at 1270cm⁻¹, and that the bending vibration peak of guaiacyl type at 1030cm⁻¹. The streching peak of methylene at 2920cm⁻¹ occurs strongly in PAS.The absorption intensi-
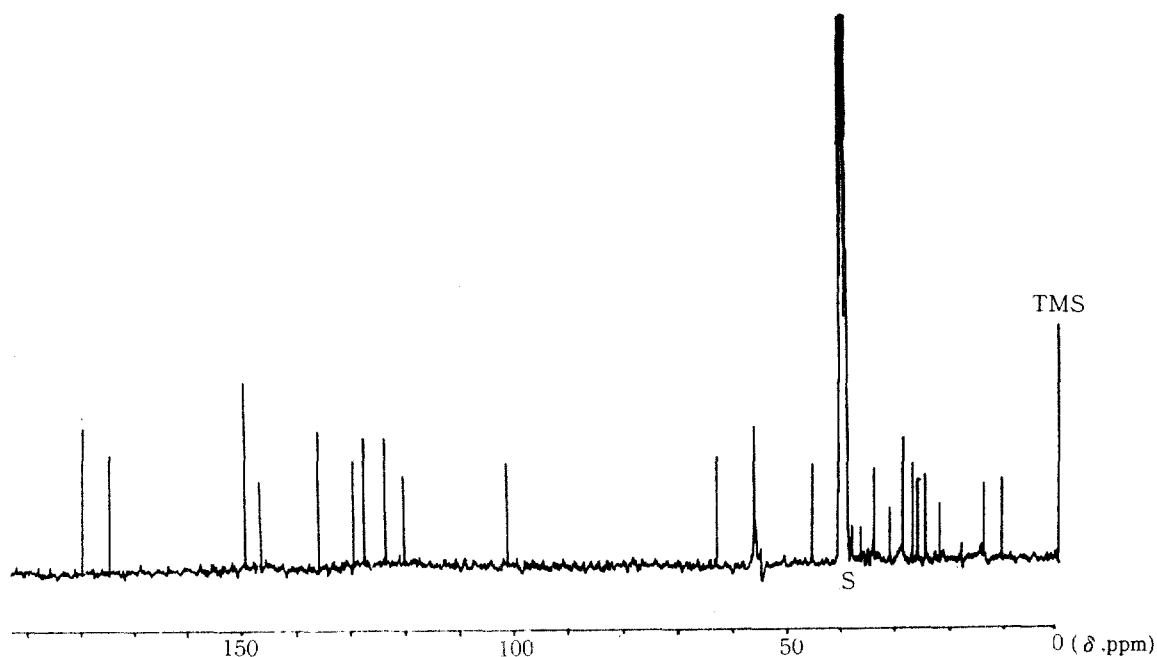
Fig. 6 ^{13}C-NMR spectrum of PAS from *Pinus densiflora* S. et. Z. S=Solvent(DMSO-d₆)

Table 7. Assignments of signals in the ^{13}C-NMR spectrum of PAS.
Chemical shifts are in δ ,ppm.

PAS δ ppm	Assignments(G=Guaiacyl)
174.574	-COOH. aliphatic(G-CHOH-COOH, G-CH₂-CH₂-COOH)
149.624	C-4 guaiacyl etherified
147.325	C-4G, etherified (β -aryl ethers, threo-form)
136.203	C-1G-CH=CH-and G-CH(OAc)-
129.687	C-1guaiacyl(C-1G-CHCH-)
127.785	C-5substituted(olefic carbons)and C-1guaiacyl
123.973	Olefinic carbons(C- β G-CH=CH-)
120.484	C-6G-CH₂-CH₂-and G-CH-
101.594	C-1carbohydrate
62.535	C- γ β -aryl ethers(erythro-form); γ -CH₂OAc
55.535	OCH₃
40.330	-CH₂-(C- α G-CH₂-COOH);-CH-
37.934	-CH₂-(C- α G-CH₂-CH₂-CH₃)
36.460	-CH₂-
34.300	-CH₂-
33.736	-CH₂-

31.367	-CH₂-(C- α G-CH₂-CH₂-CH₂OAc)
29.159	-CH₂-
26.674	-CH₂-and/or-CH₃
25.266	-CH₂-and/or-CH₃(C- β G-CH₂-CH₂-CH₃)
22.174	-CH₃
21.138	-CH₃, acetyl
14.004	-CH₃(C- γ G-CH₂-CH₂-CH₃)
10.004	-CH₃

ty of carbonyl group occurs more strongly in MCS than in PAS.

V. CONCLUSION

The methods to isolate lignin from a kraft black liquor and purify have been proposed in many ways. In the present experiment kraft lignin was isolated from a kraft black liquor and purified by Kirk's and Mörck's method. The characteristics of kraft lignin were investigated by IR and ¹³C-NMR spectroscopy. The results are as follow.

1. If Mörck's method is compared with Kirk's method. Mörck's method showes the characteristics of lignin better than Kirk's method.
2. Generally the signals of aromatic ring and side chain occur best in MCS. In the case of methoxyl group, the peak occurs best in KL-I.
3. The strong absorption peak of C- β occurs in KL-I.
4. The absorption peak of carbonyl group in IR spectra occurs most strongly in MCS, and the absorption peaks of guaiacyl type do at 1235 and 1270cm⁻¹.
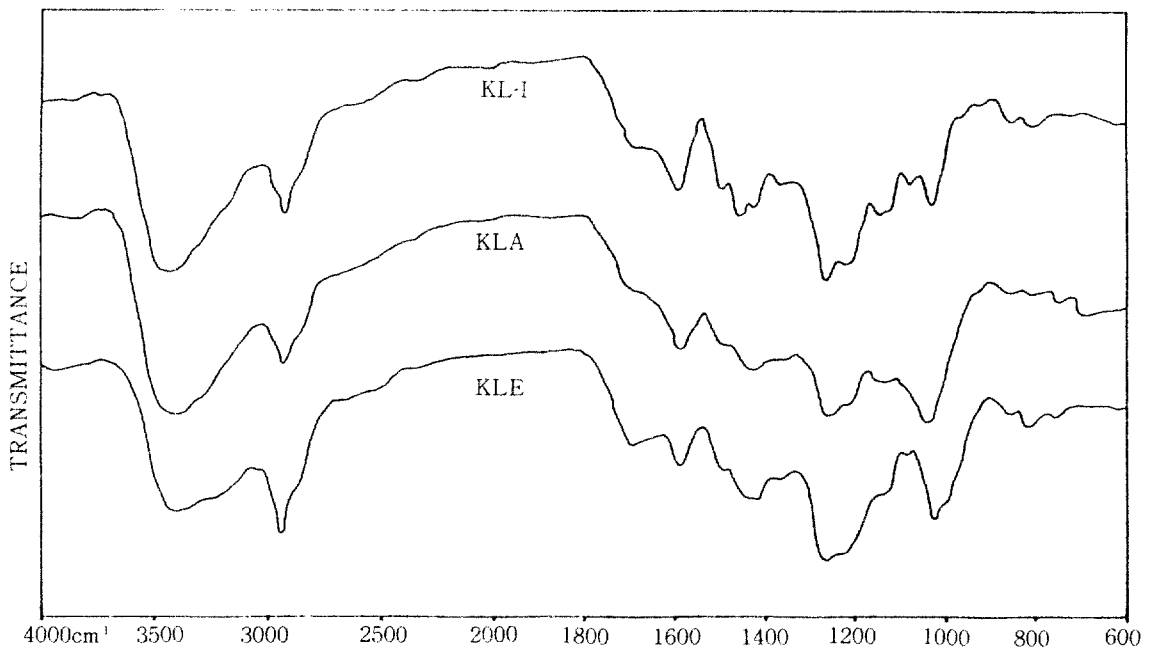

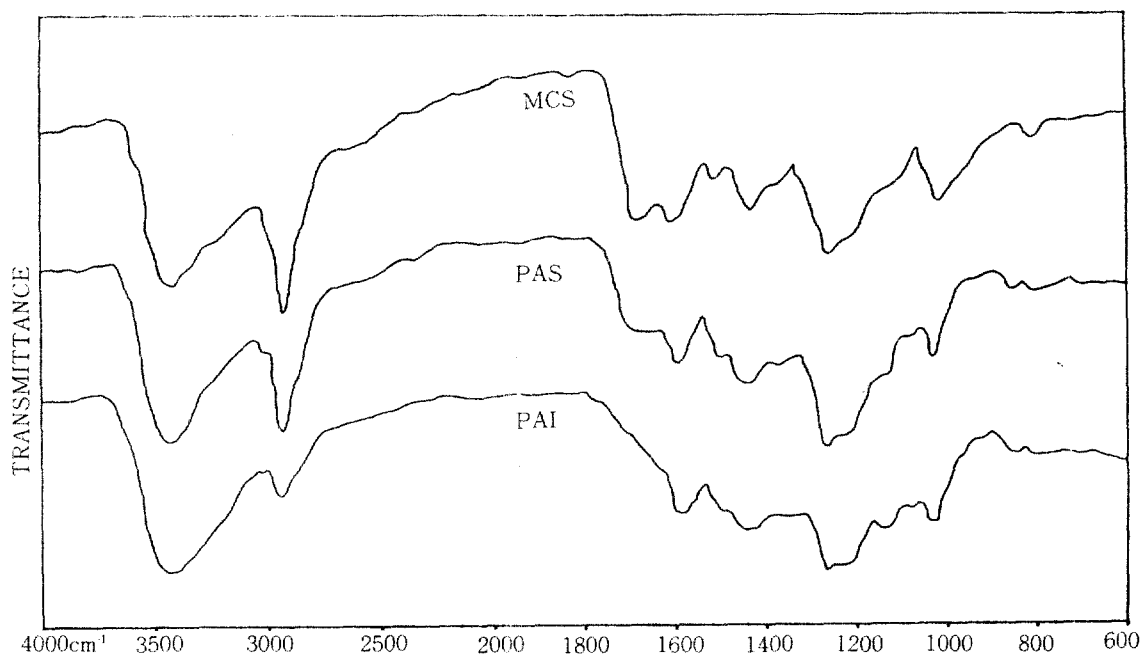Fig. 7 IR spectra of KL-I, KLA and KLE from *Pinus densiflora* S. et. Z.

Fig. 8 IR spectra of MCS, PAS and PAI from *Pinus densiflora* S. et. Z.

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