

Selective Cleavage of $C\alpha$ -Aryl Bonds in Lignin

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Summary

A novel procedure has been developed for selective cleavage of $C\alpha$ -aryl bonds in lignin. This method was termed "Phenyl Nucleus-Exchange Method" (NE-method), based on the style of reaction. The important characteristic of NE-method is to dealkylate diphenylmethane type structural units involving lignin phenyl nuclei following the formation of such structures by phenolation in the presence of acid and excess phenols. Polyhydric phenols are formed from lignin in a high yield by NE-method. In the present paper, the theory of NE-method and the degradation mechanism of lignin are outlined, and the application of NE-method for natural polyphenols and related substances is described.

Introduction

Petroleum is a fossil material and in the future it will have become either exhausted or so scarce that it will be too expensive. Therefore, the attention to alternative sources for chemical feedstocks has been directed. Coal, oil sand, oil shale and biomass have become of major interest lately. Of these sources, considerable emphasis is being given to forest biomass, wood, because wood is the most abundant and widely used renewable resource. The technology for producing basic chemical substances from cellulose and hemicellulose was established decades ago. On the other hand, few degradation methods for lignin exist which give useful chemicals in large yield. Therefore, how to convert lignin to useful chemicals is of very importance for the future establishment of a wood-based chemical industry.

In order to obtain low molecular weight phenols from lignin as industrial raw materials, the reaction should be controlled so that the resulting products are simple in structure and few in number. However, lignin has various types of linkages between its building units, and the reaction with random degradation of lignin results in an extremely complex mixture of products. Therefore, to obtain industrial raw materials from lignin, $C\alpha$ -aryl bonds should be selectively cleaved without any complicated degradation of the side chains. Because the structure of lignin phenyl nucleus is relatively simple: Softwood lignin can be regarded as a three dimensional polymer consisting of only guaiacyl nucleus.

We have developed a novel procedure, the phenyl nucleus-exchange method (NE-method)¹⁻¹⁴⁾, which allows $C\alpha$ -aryl bonds to be cleaved selectively and almost quantitatively and the phenyl nuclei to be liberated finally as polyhydric phenols. The NE-method can not only be applied for the utilization of natural polyphenols and related substances, but also gives new information

on chemical structures of natural polyphenols.

NE-Method for selective cleavage of C α -aryl bonds

Theory

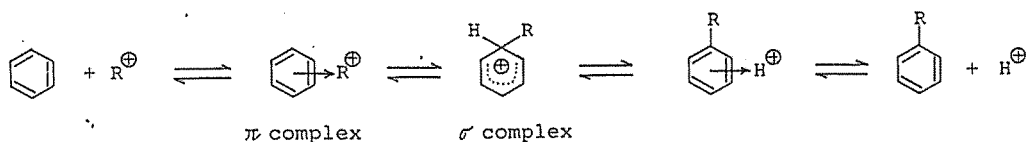


Fig. 1 Alkylation mechanism of aromatic compounds.

Fig. 1 shows the alkylation mechanism of an aromatic compound. Each reaction step is reversible. That is, alkylation and dealkylation can take place simultaneously in a reaction system. Of course, dealkylation occurs only under more drastic conditions than alkylation. However, in diphenylmethane type (DPM) compounds in which cations formed by the dealkylation are stabilized by resonance, the dealkylation energy is lower, and consequently the dealkylation occurs under milder conditions (Fig. 2). On the other hand, as alkylation and dealkylation occur

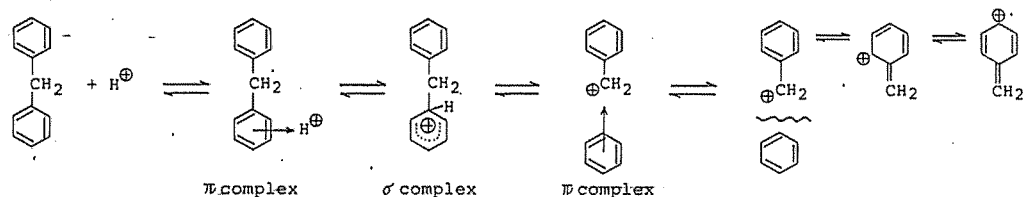


Fig. 2 Dealkylation of the phenyl nuclei in diphenylmethane type structures.

simultaneously and the rate of alkylation is more rapid than that of dealkylation, cations formed by dealkylation unavoidably recombine with phenyl nuclei, and consequently the reactants are polymerized in a complex way to give resin-like substances. However, if other aromatic compounds in large excess are present in the reaction system, newly formed cations have a higher probability to be stabilized by the other aromatic compounds and accordingly, the dealkylated phenyl nuclei remain stable as monomers in the reaction system (Fig. 3).

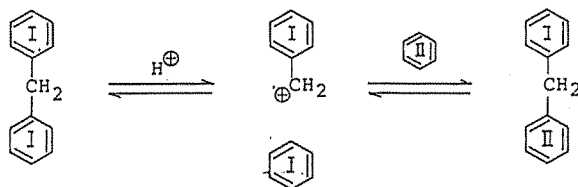


Fig. 3 Dealkylation of the phenyl nuclei in the presence of excess aromatic compounds.

The important characteristic of NE-method is to dealkylate DPM structural units involving lignin phenyl nuclei following the formation of such structures by phenolation in the presence of acid and excess phenols. That is, the NE-method consists of following three reaction

steps :

First stepFormation of DPM structures involving lignin phenyl nuclei by phenolation.

Second stepExchange of the phenyl nuclei of lignin for phenols (Phenyl nucleus-exchange reaction, NE-reaction).

Third step Demethylation of methoxyl groups.

These three reactions proceed simultaneously in the single reaction system (Fig. 4). The first and

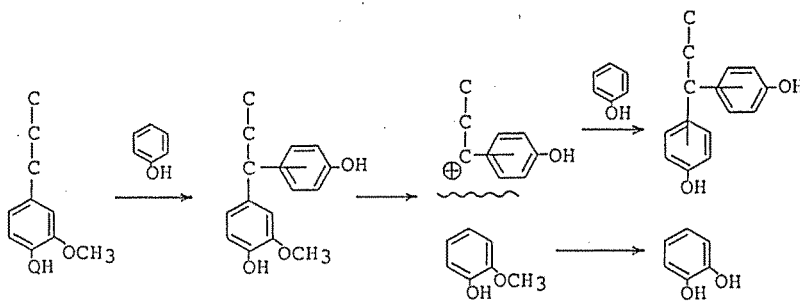


Fig. 4 Formation of catechol from softwood lignin by NE-method.

second steps proceed very fast at room temperature, and ether linkages are also cleaved rapidly with these reactions. On the other hand, the demethylation rate of methoxyl groups is much slower, compared with those of the first and second steps; and consequently it is the rate determining step in the formation of polyhydric phenols from lignin.

Monomer products from lignin by NE-method, NEP, are guaiacol and/or catechol in softwood lignin, and pyrogallol-1,3-dimethyl ether, Pyrogallol-1-methyl ether and/or pyrogallol in hardwood lignin.

Standard degradation method giving the maximum amount of NEP (Standard NE-method)

Reagent

Nineteen parts of phenol, 3 or 4 parts* of boron trifluoride-phenol complex ($\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$), and 10 parts of xylene are homogeneously mixed and stored in the absence of moisture.

* 3 parts for lignin preparations, 4 parts for protolignins.

Boron trifluoride acts as a catalyst in the three reaction steps. Although each of the steps proceeds effectively in the presence of boron trifluoride whose number (moles) is less than that of the reactive sites, the reaction system has to be controlled so that the mole ratio of water to boron trifluoride is less than one because boron trifluoride is inactivated by water included in the degradation reagent or formed during the reactions.

Phenol plays an important role as the solvent for reactants and products and as the acceptor of cations.

Xylene is a diluent.

Procedure

Lignin (or wood meal) and the reagent are placed in a stainless steel bomb and sealed [Lignin (or Wood meal) : Reagent, 1 : 35]. The mixture is heated by means of an oil bath under the prescribed reaction conditions. The mixture is cooled to room temperature, and is vigorously stirred with excess ethyl ether. The ether insoluble substances are filtered off and washed with ethyl ether. The filtrate and washings are combined and vigorously stirred with excess water saturated with sodium chloride. The ether layer is separated and dried over anhydrous sodium sulfate.

Determination of products

The reaction products in the ether solution are converted to their trimethylsilyl derivatives by treating with N, O-bis(trimethylsilyl) acetamide at room temperature for 1 hr and are analyzed by gas chromatography.

Apparatus : YANAGIMOTO G-180 instrument, Column : 30% Silicone DC-430 on Chromosorb WAW, stainless steel 3 mm ϕ \times 2 m, Column temperature : 200 $^{\circ}$ C, Carrier gas : Helium, Detector : FID.

Lignin building units giving NEP

The cleavage of C α -aryl bonds by NE-method is selective to DPM structures. Therefore, the lignin building units which originally possess DPM structures or are capable of reacting with phenol to form such structures give NEP.

The reaction sites in side chains for phenol are aliphatic hydroxyl groups, carbonyl groups, carboxyl groups, double bonds and ether bonds. Therefore, the lignin building units which give NEP almost quantitatively are non-condensed types and diphenylmethane types, and each of these units has any of the benzyl alcohol, the benzyl ether, the conjugated double bond, the α -carbonyl group, and the C α -aryl bond, in the side chain (Fig. 5).

NEP Yield

Figures 6, 7 and 8 show the NEP yields from larch- and beech dioxane lignins and Hinoki protolignin, respectively.

In larch dioxane lignin, the main product below 100 $^{\circ}$ C is guaiacol, the yield of which increases with rising temperatures up to 130 $^{\circ}$ C, above which guaiacol is demethylated rapidly to give catechol. The sum of both products increases only slightly above 130 $^{\circ}$ C, and its maximum is in fair agreement with the number of non-condensed units capable of forming DPM structures.

In beech dioxane lignin, the degradation behavior of guaiacyl units is similar to that of softwood lignin. For products from syringyl units, the yield of pyrogallol-1, 3-dimethyl ether increases with rising temperatures up to 80 $^{\circ}$ C, above which the yield decreases rapidly, accompanied by the formation of pyrogallol-1-methyl ether and pyrogallol. This is due to the beginning of the demethylation of methoxyl groups. However, the yield of pyrogallol above 100 $^{\circ}$ C is slight because of its secondary condensation, and consequently, the sum of the products decreases

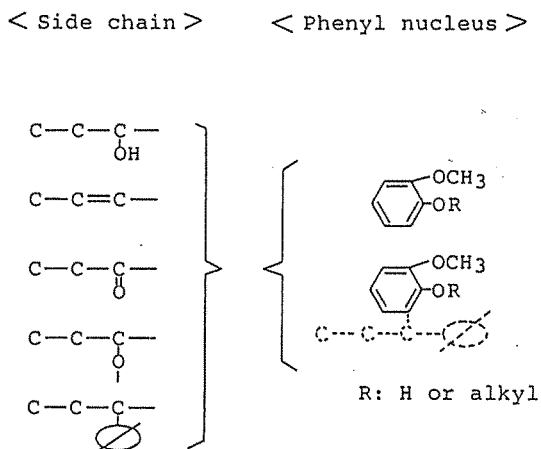


Fig. 5 Lignin building units giving guaiacol and/or catechol almost quantitatively by NE-method.

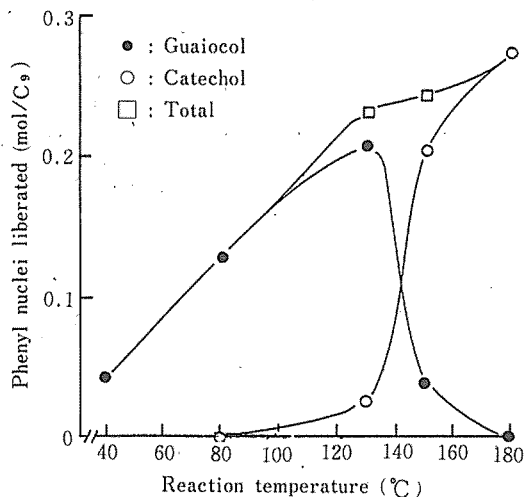


Fig. 6 Liberation of the phenyl nuclei from larch dioxane lignin by standard NE-method. Reaction time : 4 hrs.

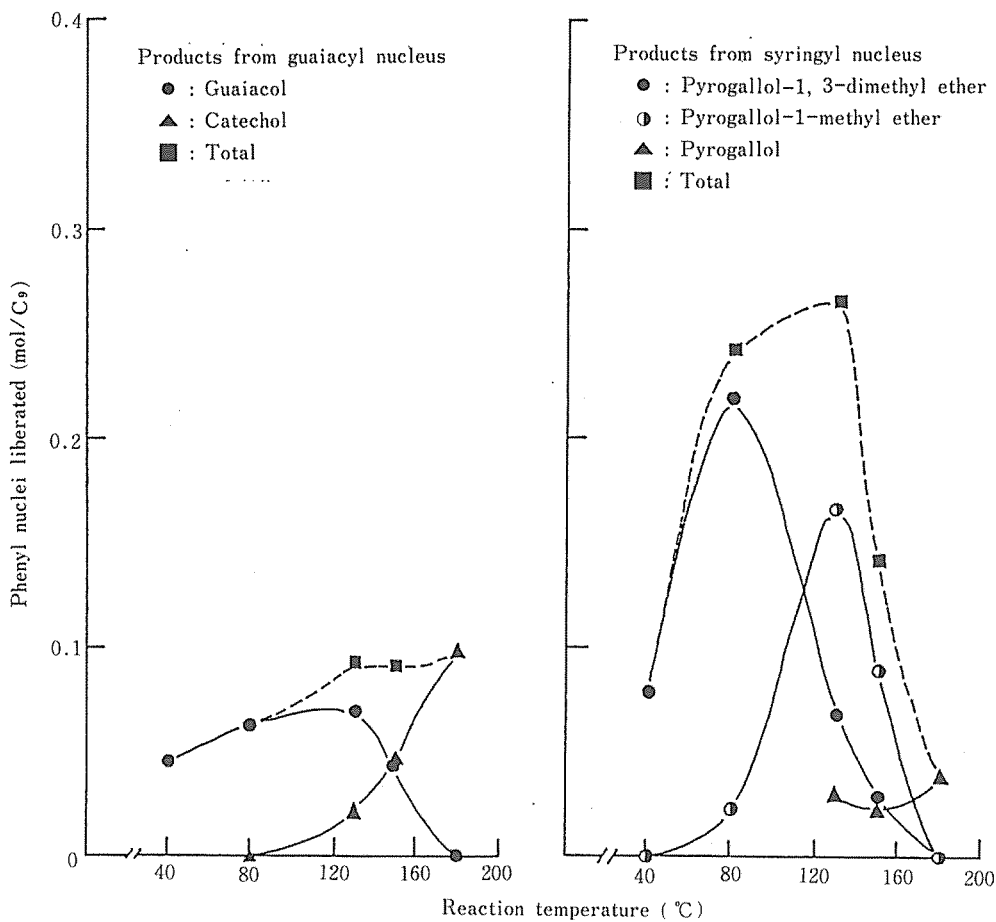


Fig. 7 Liberation of the phenyl nuclei from beech dioxane lignin by standard NE-method. Reaction time : 4 hrs.

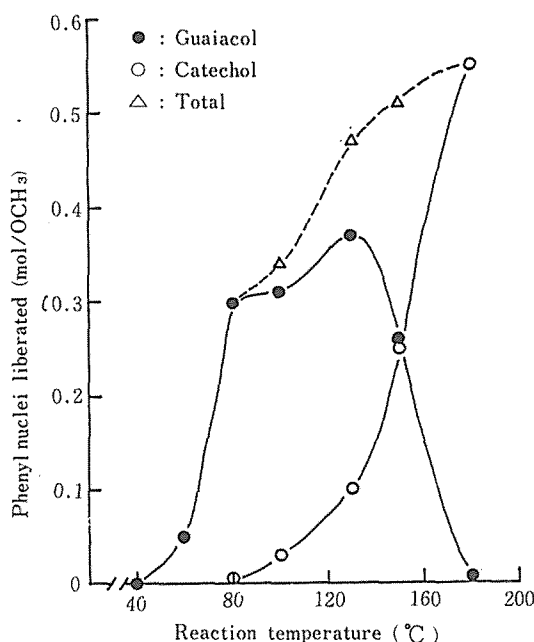


Fig. 8 Liberation of the phenyl nuclei from Hinoki protolignin by standard NE-method.
Wood meal : 80 mesh pass.
Reaction time : 4 hrs.

rapidly above 130°C, although they increase at temperatures approaching 130°C.

The degradation behavior of protolignin below 130°C is very similar to that of lignin preparations (Figures 6 and 8). Although total NEP yield increases only slightly above 130°C in the case of lignin preparations, it increases largely above 130°C in protolignin, indicating that the liberation of phenyl nuclei is still in progress. However, the exchange of the phenyl nuclei of lignin for phenol is complete under the condition at 180°C for 4 hrs, as the NEP yields are the same for the reaction times of 4 and 6 hrs at 180°C.

The NEP yields from various protolignins and lignin preparations are shown in Tables 1 and 2, respectively. The NEP yields from protolignins are in the range of about 0.45–0.55 mol/OCH₃, indicating that the condensation degree of protolignins is approximately 50% (See next section). It is worth noting that the phenyl nuclei of VANILLEX N, a residue after the production of vanillin, are liberated as monomers in about 10% yield. Non-lignin substances contained in technical lignins retard the demethylation rate of methoxyl groups, but have little effect on the liberation of the phenyl nuclei.

Degradation mechanism of lignin

The degradation mechanism of lignin by standard NE-method is as follows at each reaction temperature.

Table 1 NEP Yields from softwood protolignins.

Sample		NEP Yield*	
		% of Klason lignin	mol/OCH ₃
Spruce	<i>Picea abies</i> Karst.	28.10	0.515
Yezo spruce	<i>Picea jezoensis</i> Carr.	28.52	0.532
Glehn's spruce	<i>Picea glehnii</i> Mast.	29.84	0.551
Slash pine	<i>Pinus elliottii</i> Engelm.	25.96	0.499
Japanese red pine	<i>Pinus densiflora</i> Sieb. et Zucc.	30.42	0.570
Japanese black pine	<i>Pinus thunbergii</i> Parl.	29.30	0.519
Japanese larch	<i>Larix leptolepis</i> Gord.	24.27	0.446
Japanese fir	<i>Abies firma</i> Sieb. et Zucc.	28.04	0.507
Japanese hemlock	<i>Tsuga sieboldii</i> Carr.	27.64	0.522
Sugi	<i>Cryptomeria</i> <i>japonica</i> D. Don	28.76	0.549
Hinoki	<i>Chamaecyparis</i> <i>obtusata</i> Endl.	28.63	0.554
Japanese torreyia	<i>Torreya nucifera</i> Sieb. et Zucc.	25.39	0.465

* The sum of guaiacol- and catechol-yield by standard NE-method.
Reaction temperature : 180°C, Reaction time : 4 hrs.

—Below 50°C—

Lignin is not fully swollen by the degradation reagent at this initial stage of the reaction, because xylene, a poor solvent of lignin, is contained in large amount in the reagent. However, boron trifluoride cleaves a part of ether linkages within the lignin network to degrade lignin to smaller fragments. A part of side chains near the surface of each fragment are phenolated, especially at the α -positions, and the resulting non-condensed phenyl nuclei having DPM structures are exchanged for phenol and liberated as monomers. However, phenolation and NE-reaction scarcely occur within the fragments.

—50-100°C—

The fragmentation of lignin mentioned above proceeds to a larger degree and lignin is further swollen by phenol. Consequently, the degree of phenolation and the extent of NE-reaction increases. As a part of condensed units are separated as shown in Fig. 9, most of lignin molecules are degraded

Table 2 NEP Yields from lignin preparations.

Lignin	NEP Yield* ¹ (% of lignin)		
	Guaiacol	Catechol	Total
Larch milled wood lignin	Trace	21.4	21.4
Larch dioxane lignin I* ²	Trace	22.0	22.0
Larch dioxane lignin II* ²	Trace	19.0	19.0
TOKAI Lignin F* ³			
Original	Trace	13.2	13.2
Dialyzed	Trace	13.9	13.9
TOKAI Lignin BL* ⁴			
Original	2.4	9.0	11.4
Dialyzed	1.6	9.2	10.8
TOKAI Lignin BMN* ⁴			
Original	1.4	7.7	9.1
Dialyzed	1.8	9.1	10.9
SANX P201* ⁵			
Original	2.1	2.0	4.1
Dialyzed	2.8	6.4	9.2
VANILLEX N* ⁶			
Original	2.8	6.7	9.5
Dialyzed	Trace	10.2	10.2

*1 Standard NE-method.

Reaction temperature : 180°C, Reaction time : 4 hrs.

*2 Prepared by successive acidolysis.

Acidolysis time : I, 1 hr ; II, 2.5 hrs.

*3 Technical kraft lignin.

*4 Technical kraft lignin sulfonated.

Sulfonation degree : BL < BMN.

*5 Composed mainly of lignin sulfonate.

*6 Technical lignin sulfonic acid modified by heating with alkali.

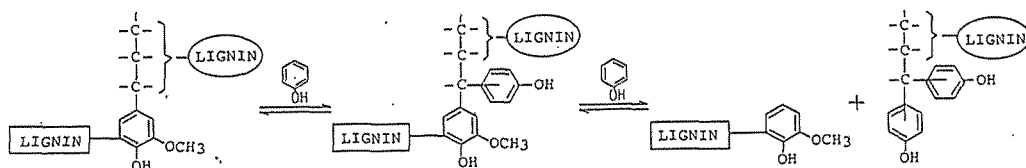


Fig. 9 Behavior of condensed type units in NE-method.

to ether soluble oligomers. The formed DPM units begin to be partly oxidized to give mesomeric quinonemethides.

—Above 100 °C—

The reactions below 100 °C proceed rapidly at the initial stage of the reaction. The units having α -carbonyl groups, which are scarcely phenolated below 100 °C, are also degraded.

Therefore, the amounts of liberated phenyl nuclei increase with rising temperatures up to 130°C. However, each fragment becomes very rigid in spite of its low molecular weight at the initial stage of the reaction because quinonemethides derived from DPM structures form strong hydrogen bonds to the adjacent hydroxyl groups of the phenol nuclei. This change of structure prevents the attack of reagents within the fragments. Also, the quinonemethides in DPM structures decrease the electron density of the phenyl nuclei and retard the formation of the π -complex between boron trifluoride and the phenyl nuclei. Thus, in fragments subjected to this change of structure, subsequent phenolation and NE-reaction scarcely occur.

Application of NE-method

The application of NE-method is not restricted only to lignin, although it was developed in order to obtain polyhydric phenols from lignin. A few examples are shown below.

(1) Activation of natural polyphenols and the production of polyhydric phenols.

Natural polyphenols such as lignins and condensed tannins are degraded to give polyhydric phenols by NE-method. For example, condensed tannins give very reactive resorcinol, phloroglucinol, catechol and pyrogallol etc. in high yield¹⁵⁾. The resulting phenol oligomers are very phenolic, and can be used as additives to plastics.

(2) Synthesis of dyes and the production of polyhydric phenols from lignin related substances.

For example, vanillin gives aurin (a triphenylmethane dye) with guaiacol by NE-method. Further, an alteration of the aromatic compound in the reaction system results in the formation of different dyes. Fig. 10 shows a possible process of lignin utilization by the combination of NE-method and oxidation method.

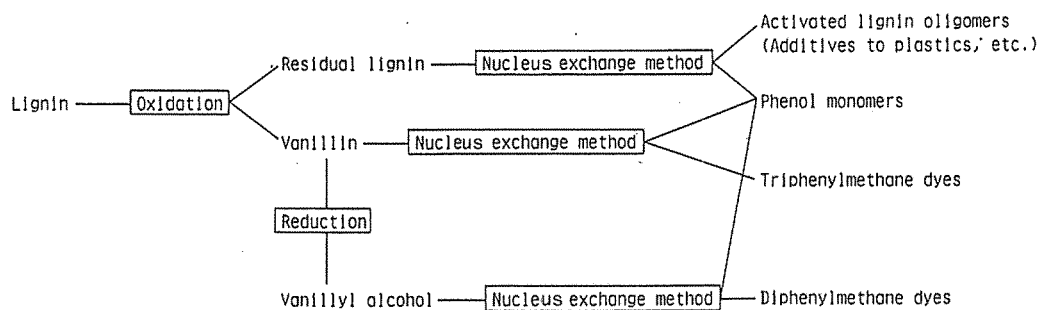


Fig. 10 A possible process of lignin utilization by combination of NE-method and oxidation method.

(3) Modification of natural polyphenols.

The properties of natural polyphenols can be modified by exchanging their phenyl nuclei for other aromatic compounds using NE-method. For example, if anillin in place of phenol is used as the degradation reagent, the property of polyphenols turns basic from phenolic.

(4) Analysis of lignin chemical structures¹⁶⁻²⁰⁾.

The NE-method gives quantitative data on the structure of original or modified protolignin without isolating lignin from wood.

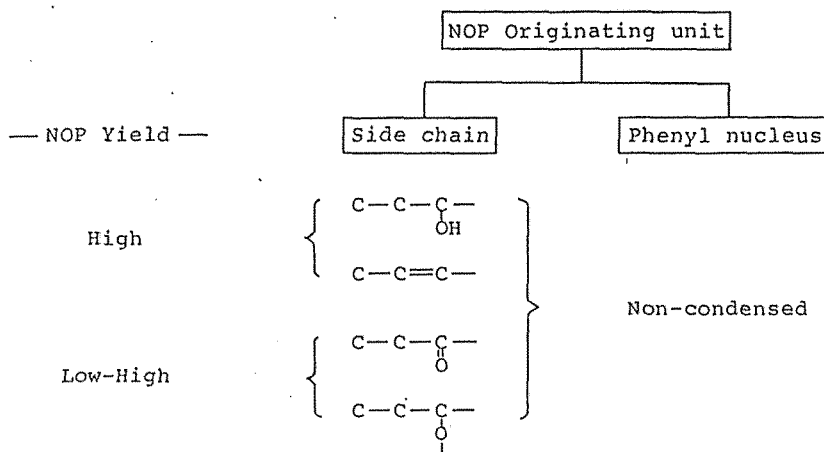


Fig. 11 Lignin building units giving aromatic aldehyde (NOP) by nitrobenzene oxidation.

Fig. 11 shows the yields of aromatic aldehydes (NOP) and their originating units in alkaline nitrobenzene oxidation. There are two significant differences between NE-method and nitrobenzene oxidation method, as obvious from the comparison of Figures 5 and 11.

- (1) The NEP is formed almost quantitatively from all originating units, whereas NOP is not.
- (2) NOP Originating units are only non-condensed types, whereas NEP originating units are both non-condensed and DPM types.

The relationship between the chemical structures of lignin and the NEP originating units and the NEP yields is compared with that on NOP in Fig. 12. In original protolignins, the NEP yield is almost equal to the number of non-condensed units. Therefore, the value of $[1-\text{NEP Yield (mol/OCH}_3)]$ is an index of the condensation degree of protolignin. NEP originating units are almost equal to NOP originating units. Thus, the ratio of NOP yield to NOP originating units can be calculated by dividing NOP yield by NEP yield. This value becomes an index for side chain structures¹⁶⁾ because it is based on the distribution of functional groups in side chains. Further, the condensation degree of *p*-hydroxyphenyl units can also be estimated using NEP and NOP. In modified protolignins or lignin preparations, the ratio of NOP yield to NEP yield becomes an index for the structural change of lignin during modification or preparation. Also, the type and the extent of condensation of lignin during such treatments can be estimated.

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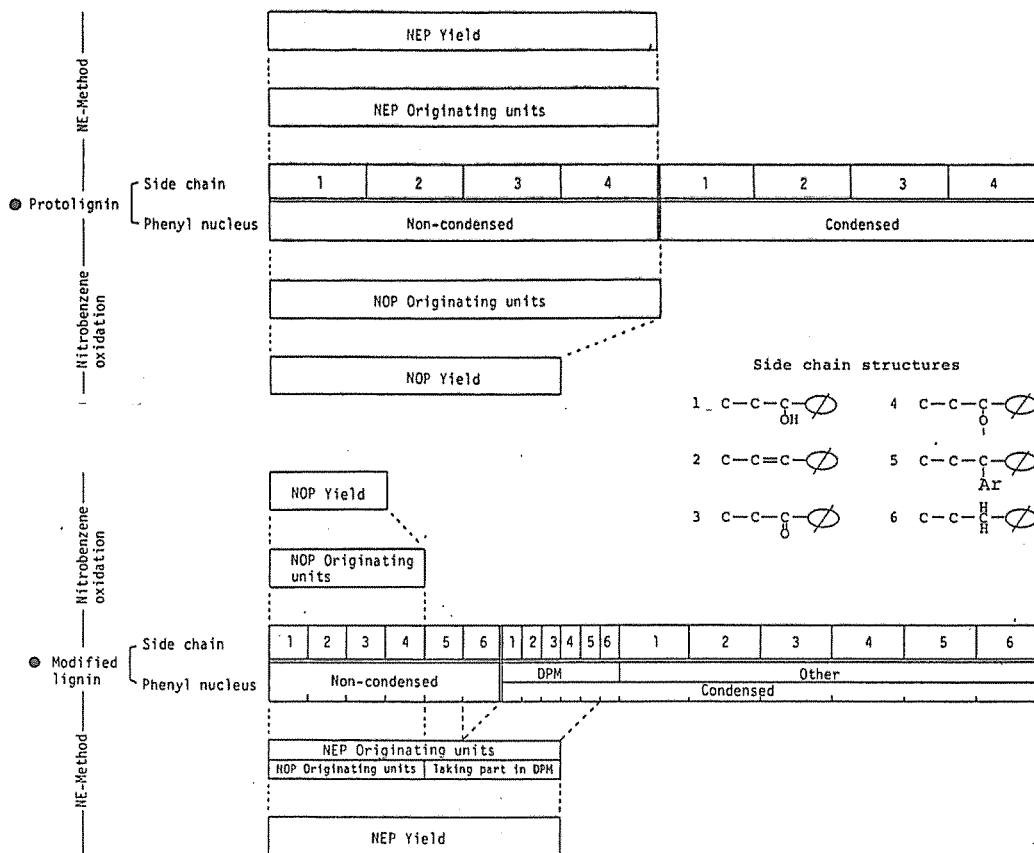


Fig. 12 Comparison between NE-method and nitrobenzene oxidation.

NEP : Phenol monomers formed by NE-method.

NOP : Aromatic aldehydes (monomers) formed by nitrobenzene oxidation.

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リグニン側鎖－芳香核間結合の選択的開裂

船 岡 正 光・阿 部 勲

リグニンの側鎖－芳香核間結合を選択的に開裂させる新たな手法（核交換法，NE－法）を開発した。NE－法は酸および大過剰のフェノール類の存在下において，ジフェニルメタン型構造単位を選択的に脱アルキル化するものであり，また同時にメトキシル基も脱メチル化され，リグニンから最終生成物として多価フェノールが高収率で遊離する。NE－法はリグニンに限定されず，天然ポリフェノールおよび関連物質の構造研究および利用分野に広く利用することが可能である。