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DOCTORAL THESIS

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クラフトパルプの塩素漂白過程における酸化的反応のリグニン分解反応及び脱リグニン反応への影響

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TABLE OF CONTENTS

LIST OF FIGURES AND TABLES

1. Introduction

2. Evaluation of the Extent of Oxidation Reaction during Chlorine Bleaching of Pulp

3. Oxidative Cleavage of Lignin Aromatics during Chlorine Bleaching of Kraft Pulp

4. Quantitative Study on the Possible Formation of Chloroform during Chlorine Bleaching of Kraft Pulp

5. Origin of Alkane-Type Structure Detected by the Analytical Pyrolysis of Oxidized Lignins

1. INTRODUCTION

- 1.1 Preface
- 1.2. Chlorine Bleaching
  - 1.2.1. General Description on Chlorine Chemistry
  - 1.2.2. The Chemistry of Chlorine Reaction with Lignin
  - 1.2.3. Formation of Chloroform
- 1.3. Analytical Pyrolysis
- 1.4. Objectives of This Work

1.1. Preface

Over 120 years have passed since pulp and paper production in Japan began in 1872, when modern paper making technology was first introduced from Europe. Japan has grown up to be one of the most important countries in the world that have successfully developed a domestic pulp and paper industry, although the pulp productivity of the industry was greatly damaged immediately after the World War II. Annual pulp production in Japan is now the third largest in the world. Annual production of paper and paper board in Japan, as well as annual consumption per nation, is the second largest after its counterpart in the US. Different from North American and Scandinavian countries, Japan is not endowed with a vast expanse of forest as forest products resource. Japan is located far from the major countries that can furnish forest products. Japan is so small a country for its population that only small area is available for industrial use. All of these disadvantages taken into consideration, it is surprising that Japan has developed pulp and paper industry of its own as it is today. Although computer network has been rapidly developed as one of the promising alternatives, paper, or more precisely "printed matter," is still the most important communication medium in our daily life, as seen in such a saying "Paper consumption is a criteria for the civilization of a country." It is indisputable that pulp and paper industry will be playing an important role, as it is today, among a lot of industries in Japan. Shown in Figs.1-1, 1-2, and 1-3 are the changes in annual pulp production in Japan during the past six decades.[1,2]

As for its use, pulp can be divided into paper pulp and dissolving pulp. Paper pulp can be classified into mechanical pulp, chemical pulp, and the combination of the two, semichemical pulp. Chemical pulp production is outstanding in modern Japan, as

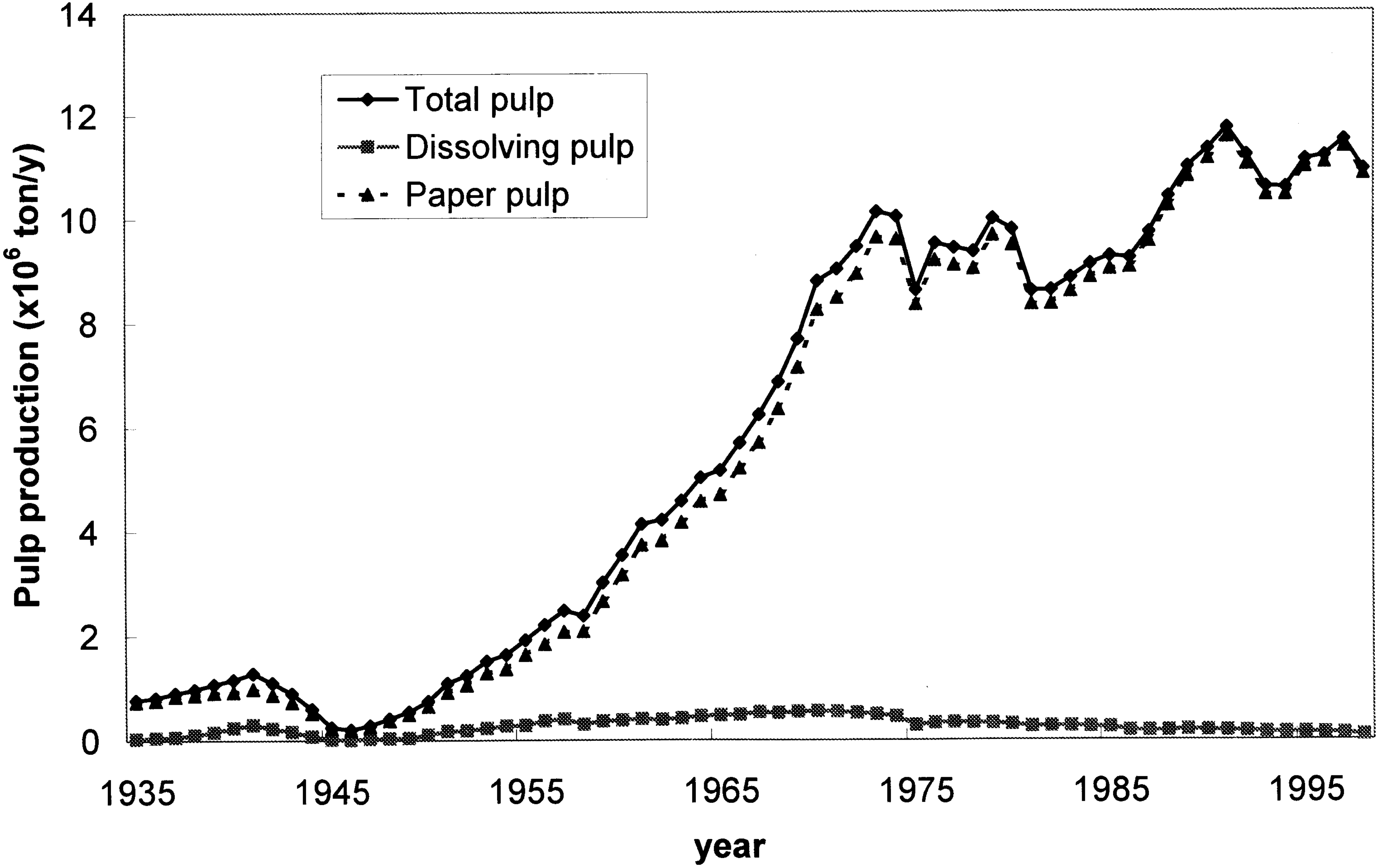


Fig. 1-1 Annual production of total pulp in Japan

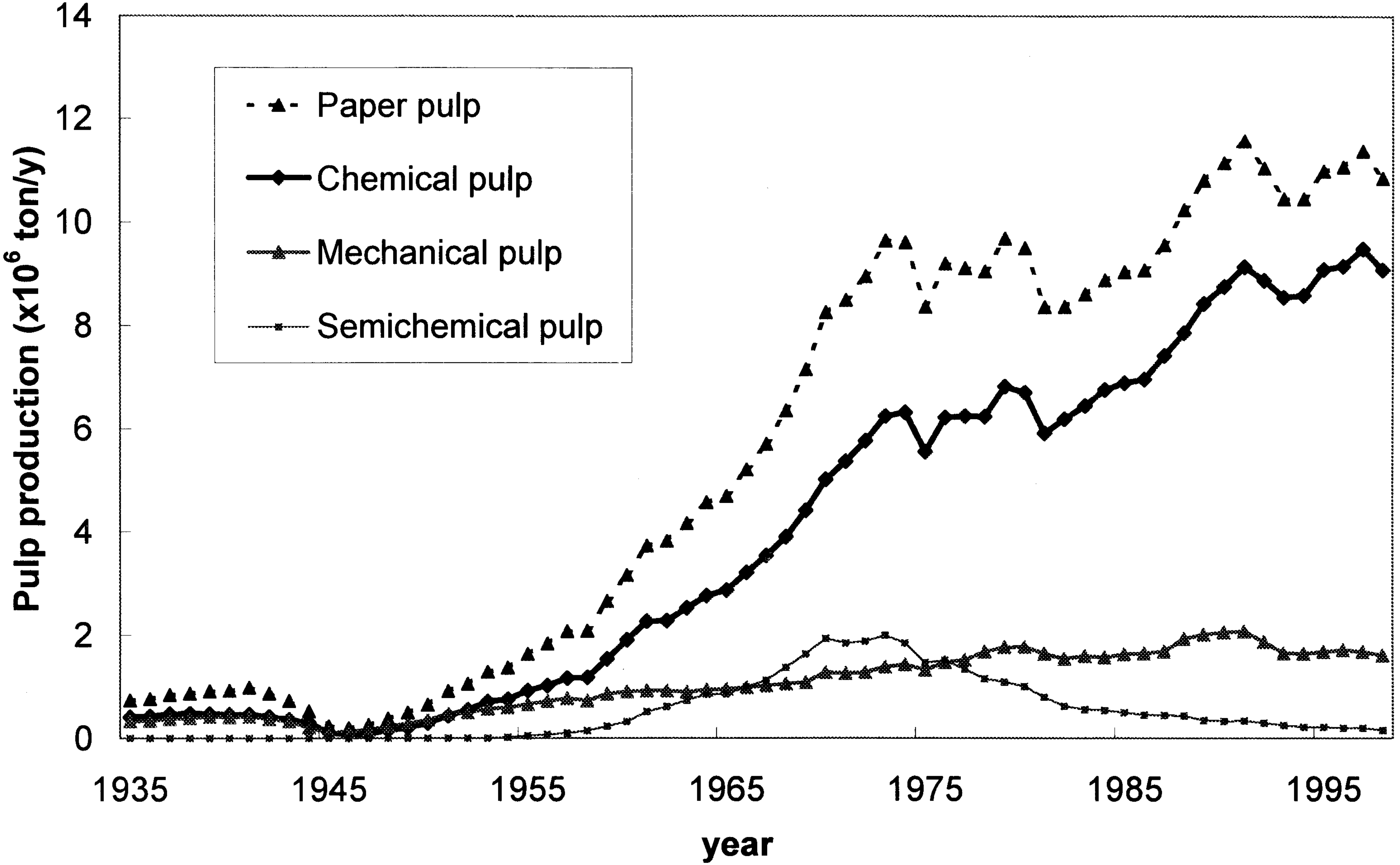


Fig. 1-2 Annual production of paper pulp in Japan

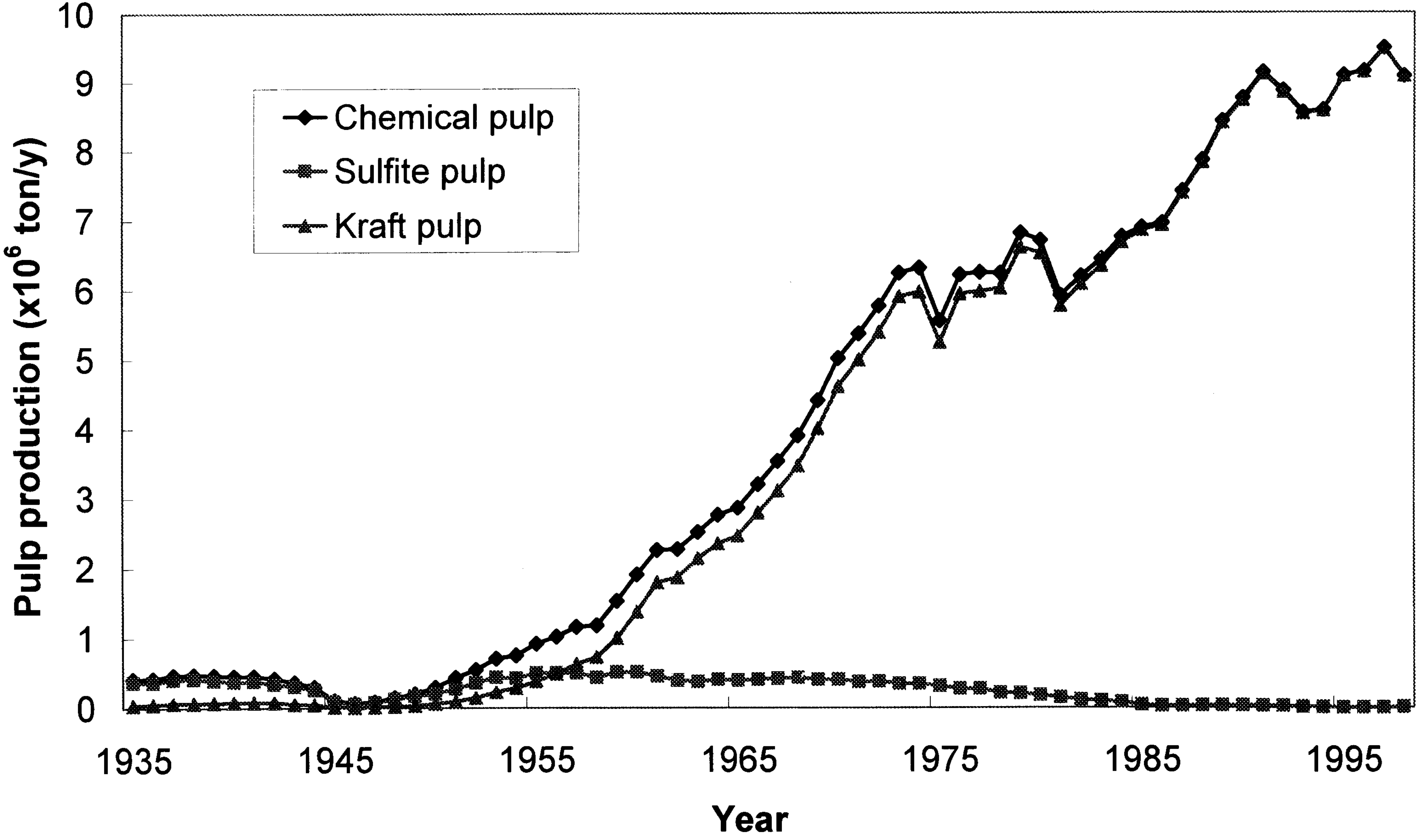


Fig. 1-3 Annual production of chemical pulp in Japan

seen in Fig.1-2. Chemical pulp is prepared as a result of defibration of wood chip by the addition of some chemicals that can remove almost all the lignin, one of the major chemical components of wood. To make wood chip into pulp, it is necessary to treat the mixture of wood chip, water, and chemicals at a desired temperature. This process is referred to as pulping process, or cooking process. Amongst chemical pulping processes, soda pulping process, using sodium hydroxide as a chemical, was the first innovation that emerged in the latter half of the nineteenth century. Sulfite pulping process, using basically sulfite and bisulfite, was later developed. Sulfite pulping process has an advantage of producing relatively bright unbleached pulp, which thus only needs relatively simple treatment to gain high brightness. Sulfite process had been the most dominating chemical pulping process until kraft pulping process, basically using sodium hydroxide and sodium sulfate, was established. Kraft process began to gain ground in around 1930, because this new process can produce better pulp strength property than sulfite process.[3] The pulp produced by kraft process (kraft pulp) shows better productivity than that by sulfite process (sulfite pulp). Kraft pulp, however, gives relatively lower brightness and/or whiteness than sulfite pulp, and therefore requires additional treatments in order to achieve a certain level of brightness if it is required. Despite this disadvantage, kraft pulping process gradually took the place of sulfite process, especially after new technologies such as chemical recovery system and chlorine dioxide bleaching process were introduced or established. Among the chemical pulping processes kraft process is, and will be, exclusively in use in pulp and paper industry in the world, since in addition to many advantages of it, the measures to reduce environmental loadings have been taken recently. This trend is seen in annual paper production in Japan (Fig.1-3). On the contrary, sulfite pulp production in Japan seems to be "on the verge of extinction." As clearly shown in

Fig.1-3, sulfite pulp production has been reduced to less than one-three hundredth during the past three decades. Sulfite process in Japan is now used mostly for the manufacture of dissolving pulp.

High molecular weight lignin is modified structurally and some parts of it are broken into smaller fragments during chemical pulping process. Lignin is, as a result, removed easily from wood chip. Over 90% of lignin in wood chip can be removed during kraft pulping process. Small portion of lignin that can not be removed in the process still exists in unbleached pulp. This is called kraft pulp residual lignin, the structure of which is modified to some extent during the pulping process under alkali condition when compared with that of wood native lignin. It is said that the dark color of kraft pulp is mainly due to the light absorption of some functional groups (chromophore) mostly in the residual lignin, rather than in the residual carbohydrates.[4,5] Normally, defibrated wood chip that underwent chemical and/or mechanical pulping processes also contains some substances causing color. Kraft pulp prepared under alkali condition shows lower brightness than sulfite pulp prepared under neutral or acidic condition. This is partly explained by the fact that some chromophore is created in lignin to a greater extent when subjected to alkali. Light absorption of kraft pulp residual lignin seems much higher than those of sulfite pulp residual lignin and wood native lignin. Therefore, kraft pulp shows dark color for its lignin content. Kraft pulp is sometimes required to gain high brightness and/or whiteness, depending on the purpose of its use. Pulp bleaching is the process which achieves high brightness with keeping other good qualities (i.e. pulp strength) within a satisfactory level. Bleachable-grade chemical pulps (i.e. paper-grade kraft pulp) needs in general complete removal of residual lignin and other chromophores. Yet all other pulps (i.e. mechanical pulp) sometimes requires breakage of chromophore, but not necessarily delignification to maintain pulp yield. The bleaching suitable for the former is generally called lignin-removing bleaching, and that for the latter lignin-retaining (lignin-preserving) bleaching.[6] In modern bleaching, both lignin-removing and lignin-retaining bleachings are thought to operate. Modern bleaching system (multistage bleaching) is composed of combinations of a variety of bleaching sequences. Multistage bleaching is employed as a common bleaching system suitable for kraft pulp bleaching, because it is very difficult to remove and break all the chromophores by a single stage bleaching. In the early stages of multistage bleaching sequences, lignin-removing bleaching seems to advance as an additional delignification process that follows pulping process. It is thought that kraft pulp undergoes lignin-retaining bleaching at the later stages rather than lignin-removing bleaching.

Oxidizing chemicals, as well as reducing chemicals, are commonly used as pulp bleaching agents. Reducing chemical agents are sometimes used to produce bleached mechanical pulp, but the use of them is very limited. Oxidizing chemicals are often used for kraft pulp bleaching. Chlorine-containing bleaching agents such as elemental chlorine (Cl_2), hypochlorite (ClO^-) and chlorine dioxide (ClO_2), have been conventionally used world-wide. Those chemicals have a large oxidation potential and known as very effective bleaching agents. They show relatively high reaction selectivity toward lignin, rather than toward carbohydrates. Using those chemicals, however, more or less leads to produce various chloro-organics inevitably, some harmful influences of which on the ecosystem are suspected. High molecular weight chloro-organics can exist persistently in the environment, only to be decomposed slowly to produce lower molecular weight organic substances. The toxicity of high molecular weight chloro-organics *per se* is not clear, but suspected to be rather lower than that of low molecular weight chloro-organics. But high molecular weight chloro-organics, when decomposed in the environment, have a probability to show relatively strong toxicity, which needs further investigation. On the surge of environmental concern, new bleaching technologies are under development. Commercial-scale use of chlorine-free, or oxygen-containing bleaching agents such as oxygen (O_2), ozone (O_3), hydrogen peroxide (H_2O_2) and other peroxides has been increasing recently. They can, if properly used, decompose and remove most of the substances causing color under a mild reaction condition.

The number of bleaching agents now available, which can attack effectively residual lignin of pulp under low operating cost, is very limited. Because of the recent interest for the environment, it is becoming an urgent project to establish a new bleaching process that can be used safely. The idea of "environmentally friendly" is often referred to in many fields of modern industries and may be somehow a cliché, but nowhere should the truth of this idea be better exemplified in the realm of pulp bleaching technology. Elementary chlorine-free (ECF) bleaching process using chlorine dioxide but not elemental chlorine, followed by the emerge of totally chlorine-free (TCF) bleaching process using no chlorine-containing materials, has been developed and applied in a plant-scale.[7] Besides, totally effluent-free (TEF) process by which no effluent emission to the environment is expected, is beginning to be employed in some plants in Scandinavian countries. Although it will take a long time for pulp and paper industries all over the world to accept the TCF process via the ECF process, chlorine-based bleaching technology will undoubtedly be substituted completely for less-chlorine or chlorine-free bleaching technology. Nevertheless, pulp and paper industry in Japan still largely depends on elementary chlorine for pulp bleaching due to its low operating cost. Generally, bleaching effluent contains rather lower organic substances and is more difficult to reuse than black liquor of kraft pulping process. Bleaching effluent is discharged to the receiving water like river, lake and the sea, after subjected to some chemical and/or biological treatments. Chlorine bleaching effluent carries a wide variety of organic substances containing chlorine (chloro-organics), part of which shows acute, or chronic toxicity[8] and mutagenicity.[9-17] Chlorine bleaching effluent is, thus, suspected to be a heavy load to the environment. Total pulp production in Japan in 1995 is approximately 9.1×10^6ton/y (as shown in Fig.1-1), and the production of bleached pulp production accounts for about 80% of the total (7.4×10^6ton/y). If one assumes that bleaching effluent contains 1.0kg/t (on dry weight basis of brown stock) of AOX (Adsorbable Organic Halides), one can give an approximate estimation on the degree of its emission to the environment (i.e. approximately 7×10^3ton/y as AOX and 2×10^4-5×10^4ton/y as total chloro-organics). The long-term influence of a lot of chloro-organics on the ecosystem, however, is still unknown, and should be made clear. More basically, the reaction between chlorine and lignin has been investigated by many researchers, but the whole knowledge of it is yet to be clarified. It seems more and more important to make better understanding of it in order to establish a new bleaching technology, a new treatment system for the effluent, and a new analytical procedure for the approach to the long-term behavior of chloro-organics in the environment.

1.2. Chlorine Bleaching

1.2.1. General Description of Chlorine Chemistry

General description of chlorine chemistry mentioned in this section is based on the summary of previous studies and review articles.[18-20]

Chlorine exists as greenish-yellow, diatomic gas at ambient temperature. Chlorine has been in wide use after discovered by Scheele in 1774. But chlorine is a very hazardous, irritant chemical which may sometimes cause injury or even death.

In an industry-scale production, chlorine is obtained at the anode surface by electrolysis of aqueous sodium chloride. In laboratory, chlorine gas can be evolved by the addition of hydrochloric acid to manganese dioxide.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + H_2O$$

Gaseous chlorine is about 2.5 times higher in density than air. The aqueous solubility of chlorine strongly depends on the temperature, showing fairly high aqueous solubility. A saturated chlorine water prepared at room temperature, for example, contains 5-10g/l as active Cl_2. When a saturated chlorine water is put under low temperature (i.e. below 10°C), chlorine combines with water to form crystalline hydrates ($Cl_2 \cdot 8H_2O$). Chlorine itself works as a strong oxidant. Chlorine is hydrolyzed in aqueous solution to form hypochlorous acid (HClO), which works as a weak acid and a strong oxidant.

$$Cl_2 + H_2O \rightleftarrows HCl + HClO$$

Hypochlorous acid can be converted to dichlorine monoxide according to the following equilibrium.

$$2HOCl \rightleftarrows Cl_2O + H_2O$$

It is known that this equilibrium is attained so slowly that the formation of dichlorine monoxide is very limited. But in a certain reaction condition (i.e. within the pH region below 7.5), the presence of dichlorine monoxide may have to be taken into account. Unfortunately, the significance of this compound is not known very well.

When gaseous chlorine is introduced to sodium hydroxide solution, sodium hypochlorite is produced.

$$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$$

Hypochlorite (ClO^-) is one of the most popular oxidizing agents. Bleaching powder, or calcium hypochlorite, CaCl (ClO), has been widely used from the early history of fiber bleaching because this agent is easier to prepare, handle and transport than gaseous chlorine. It is dissociated in aqueous solution as follows.

$$CaCl(ClO) \rightarrow Ca^{2+} + Cl^- + ClO^-$$

Hypochlorite was the only bleaching agent for rags and other fibers used for papermaking as raw materials, until elementary chlorine was commercially applied as a bleaching agent for pulp.

Hypochlorite can react with hypochlorous acid under neutral condition to form chlorate (ClO_3^-).

$$ClO^- + 2HClO \rightarrow 2H^+ + 2Cl^- + ClO_3^-$$

This reaction is applied to industrial production of chlorate. Chlorate does not react with pulp components unless a strong acid condition is used.

Chlorine is usually used as aqueous solution for bleaching of pulp, called chlorine water. Chlorine is dissolved in water to hydrolyze as follows:

$$Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HClO \qquad [1]$$

In aqueous solution, hydrogen chloride is almost completely dissociated to form chloride and proton. Hypochlorous acid, as a weak acid, is in equilibrium as follows:

$$HClO \rightleftarrows H^+ + ClO^- \qquad [2]$$

It is known that equilibrium constants K_1 and K_2 for these reversible reactions [1] and [2] respectively are dependent on temperature. It is reported that at 25°C the values of K_1 and K_2 are $3.9x10^{-4}$ and $5.6x10^{-8}$, respectively. Higher temperature and higher pH of the chlorine water, shifts the equilibrium more greatly to the direction in which hydrolysis of chlorine proceeds. The pH dependence of chlorine water is known in previous studies.[21] Below pH 1, elemental chlorine (Cl_2) is predominant over any other active chlorine species. In the pH range of 4 to 6, hypochlorous acid (HClO) is exclusively the main active chlorine. Within the pH region over 9, hypochlorite ion (ClO^-) accounts for almost 100% of the active chlorine species. It is also known that chlorine consumption by lignin is dependent upon the reaction temperature. It is, thus, worthy to note that the reaction conditions such as pH and temperature greatly affect the reactivity of chlorine toward substrates.

Elementary chlorine (Cl_2) is essentially a polarized molecular ($^{\delta+}Cl\text{-}Cl^{\delta-}$), and can easily provide chloronium ion (Cl^+) in acidic aqueous solution when it reacts electrophilically with a substrate because chloride (Cl^-) is one of the best leaving groups. When chlorine attacks aromatic substances such as lignin, it cleaves a carbon-hydrogen bond. As a result, a carbon-chlorine bond is newly formed. Generally, the carbon-chlorine bond in aromatic substances is relatively stable so that mild alkali treatment can not achieve complete dechlorination. In addition, it is known that some highly chlorinated, toxic organic compounds (i.e. PCBs) are supposed to be bioaccumulative. Therefore, some of chloro-organics, when discharged to the environment as industrial wastes, persistent in the ecosystem. This suggests it is difficult to convert them to less toxic substances for a short period of time.

It is known that in a gas state, chlorine can either attack substrates as a molecular species or react with them after decomposed to chlorine radicals. Especially under the influence of light, chlorine is spontaneously decomposed to radical species as a result of homolytic cleavage, as observed for other halogens.

$$Cl_2 \rightarrow 2Cl\cdot$$

Chlorine radical can also be formed when molecular chlorine attacks substrates to abstract a hydrogen radical to form hydrogen chloride, although this process is said to be slow.

$$Cl_2 + RH \rightarrow Cl\cdot + R\cdot + HCl$$

Once formed, chlorine radicals can initiate a rapidly accelerating chain reaction as shown below.

$$Cl\cdot + RH \rightarrow R\cdot + HCl$$

$$Cl_2 + R\cdot \rightarrow RCl + Cl\cdot$$

It has been assumed that reaction of chlorine with carbohydrates proceeds mainly via radical formation, for the reaction can be successfully retarded in the presence of some radical scavengers, such as chlorine dioxide.

$$Cl\cdot + ClO_2\cdot + H_2O \rightarrow Cl^- + ClO_3^- + 2H^+$$

But in aqueous solution, the influence of this radical reaction seems minor unless excessive amount of chlorine is added.

1.2.2. The Chemistry of Chlorine Reaction with Lignin

In the conventional multistage bleaching processes of kraft pulp, chlorination stage (C-stage) is basically taken place as a first bleaching stage in the sequence, followed by alkali extraction stage (E-stage). Kraft pulp residual lignin is attacked by chlorine in C-stage so that the complicated structure of the lignin can be modified to form a lot of acidic group, which becomes labile to the successive alkali treatment. In E-stage, the most of modified residual lignin is dissolved in aqueous solution and thus removed to produce a pulp with a low kappa number. This is why C-stage combined with E-stage is sometimes referred to as an additional delignification process after pulping. Hypochlorite bleaching stage (H-stage), chlorine dioxide bleaching stage (D-stage), and hydrogen peroxide bleaching stage (P-stage) basically follow the two stages to obtain brightness required.

Countless attempts have been made in the past several decades to clarify the bleaching chemistry of chlorine. Of so many researches that it is almost impossible to arrange them all systematically, some outstanding works are selected and presented here. The researchers group of Sarkanen, Dence and co-workers produced a lot of intensive reports to propose the reaction mechanisms in relation to chlorine treatment.[22-29] Using lignin model compounds, they illustrated lignin solubilization process both by degrading the lignin macromolecules and by increasing their hydrophilic nature.[22] The reaction of chlorine with lignin such as substitution reaction and dealkylation reaction, and the feature of chlorolignin are extensively investigated.[23-29] Solubilization mechanism of lignin during chlorine bleaching was reported by many researchers.[30,31] The reason for less bleachability of kraft pulp than that of sulfite pulp was also investigated.[32-36] Kondo and co-workers[32,37] tried to approach to the factors that are responsible for the difficulty in bleaching of kraft pulp. They investigated characteristics of some bleaching chemicals.[38] They also made some attempts to understand the mechanisms of lignin removal during chlorination and alkali extraction stages.[37,39-43] Kawachi and co-workers[37,39-43] put an emphasis on the assumption that the three-dimensional network structure of lignin is loosened by chlorine to form new hydrophilic groups at the cleavage position of the molecule, which can be dissolved in alkaline solutions. Together with many other studies, representative reaction patterns of chlorination have been slowly but steadily clarified. Postulated reaction patterns between chlorine and lignin falls into some categories as follows;

1. substitution reaction and electrophilic displacement reaction
2. oxidation reaction
3. catalytic hydrolysis reaction
4. electrophilic addition reaction to carbon-carbon double bond

In aqueous solution, all of these reactions are essentially initiated by the electrophilic attack of chlorine against the substrate. Amongst these reactions, chlorine does not lose its oxidation power during catalytic hydrolysis reaction process though the reaction is closely related to structural modification of lignin. Other reaction processes consume oxidization power of chlorine.

Substitution reaction, such as electrophilic aromatic substitution reaction, is a representative reaction of chlorine. Chlorine, or chloronium ion, attacks electron-rich lignin aromatics. Substitution reaction and electrophilic displacement reaction are essentially the same type, since in these processes, one mole of organic chloride and one mole of inorganic chloride are produced from one mole of elementary chlorine. But electrophilic displacement reaction occurs only when lignin side chain carries α-hydroxyl group. The side chain is eliminated in this process to form aldehyde. If this reaction occurs, lignin macromolecule is greatly converted to low molecular substances. This is the reason this reaction has been thought to be one of the main reactions deeply involved in lignin degradation and thus delignification of pulp. Aromatic substitution itself does not seem to contribute the increase in aqueous solubility of lignin, but if chlorine attached to the lignin aromatic ring is substituted for hydroxyl group by the following alkali treatment, lignin macromolecule increases its solubility in water. It can, thus, be said that aromatic substitution reaction indirectly helps to increase lignin solubility in aqueous solution.

Oxidation reaction is assumed to be one of the most important reactions during chlorine bleaching, because aromatic structure of lignin can be greatly modified by this reaction to form muconic acid derivatives via ortho-quinone structure. It is thought that this reaction is also related deeply to the degradation and/or removal of lignin, because it can add the hydrophilicity to lignin macromolecule even when the complicated three-dimensional network of lignin structure is not broken completely. As a result of this reaction, modified lignin structure becomes labile to the following alkali treatment. It can be said that this reaction directly helps increase in aqueous solubility of lignin. Two moles of chloride are formed from one mole of elementary chlorine in this process.

Catalytic hydrolysis by elementary chlorine is also important, since this is also deeply involved in the modification of lignin structure. Almost all the ether bondings that survived kraft pulping process can be cleaved by this reaction. Methanol liberation is observed as a result of demethoxylation. No chlorine loses its oxidation power in this process.

Electrophilic addition reaction by elementary chlorine is also important when lignin side chain has the carbon-carbon double bond. Ideally, no chloride is formed from one mole of chlorine in this process. If the reaction between lignin and chlorine occurs in a gas phase, the addition reaction is postulated to proceed to a substantial degree via a radical reaction mechanism. Chlorine is usually, however, used in an aqueous solution, suggesting that the reaction by chloronium ion rather than such a radical reaction easily proceeds. In an aqueous solution, addition reaction by chloronium ion to the carbon-carbon double bond is followed by the nucleophilic attack by the lone pair of oxygen atom in water molecule, resulting in the formation of chlorohydrin. If trace amount of water exists, chlorohydrin is expected to be produced via electrophilic addition of chloronium ion to carbon-carbon double bond even when non-porous solvent is used for chlorination of lignin. Consequently, one mole of organic chloride and one mole of inorganic chloride are produced from one mole of elementary chlorine in this process, which seems similar in the case of substitution reaction.

Therefore, representative reaction pattern shown above can be reclassified into three categories as follows.

[A] substitution type: one mole of Cl_2 is consumed by the substrates to form one mole of Cl^-

[B] oxidation type: one mole of Cl_2 is consumed by the substrates to form two moles of Cl^-

[C] catalytic hydrolysis type: no Cl_2 is consumed by the substrates

Reaction types [A] and [B] come within the scope of the discussion in chapter 2, by determining the formation of chloride (Cl^-). In chapter 3, reaction type [C] is mainly focused on.

1.2.3. Formation of Chloroform

It is a well-known fact that an enormous amount and a wide variety of low molecular weight organic compounds are formed as by-products and discharged to the environment from bleaching process.[44,45] Chloroform is one of the most abundant compounds produced at bleach plants.[46-48] The compound contains three organochlorine atoms in a molecule with a molecular weight of 119.38. It is known as a volatile compound (vapor pressure at 25°C is about 200mmHg) with a boiling point of 62°C. In recent years, the emission of chloroform to the environment has been of great concern in Japanese pulp and paper industry. It is assumed that the long-term inhalation of chloroform is harmful to the workers' health even if the atmospheric concentration of it is quite low. Exposure to chloroform is thought to be a potential danger because it is a suspected carcinogen.

The formation of chloroform is observed when pulp, or lignocellulosic material is treated with chlorine under alkaline condition (hypochlorite treatment). The reaction mechanism is classically known as haloform reaction. In addition, chloroform and other chlorinated methane derivatives are produced when lignin is treated by acidic chlorine water. In this case, the amount of produced chloroform is generally much smaller than that in the case of hypochlorite treatment. But if chlorine charge is large enough and if the acidic chlorine treatment is followed by alkali treatment, substantial amount of chloroform can be produced. In previous literatures, the formation mechanism of chloroform from methyl ketone structure is tentatively proposed.[49,50]

In alkaline condition, abstraction of α-proton to the carbonyl group is slow and thus rate-determinating step. But once a chlorine atom is substituted for an α-carbon atom, the next abstraction of another α-proton becomes easier than the first one. This is explained by the electron-withdrawing effect of chlorine (or more accurately, halogen). This effect renders the second elimination of α-proton easier than the first. The third elimination of α-proton proceeds much more easily. Hence, trichlorinated methane (chloroform) is predominantly produced after the trichlorinated methyl ketone structure (the precursor of chloroform) is hydrolyzed by the attack of hydroxyl ion (OH^-).

In acidic condition, the first protonation on the carbonyl oxygen is fast, and the first abstraction of α-proton is slow and thus rate-limiting step. When a chlorine atom is substituted for α-proton, the following abstraction of α-proton becomes more difficult due to its electron-withdrawing effect. Consequently, mono-chlorinated methane (methyl chloride) is obtained with high yields.

The next important step to take in the discussion of this section is how (chlorinated) methyl ketone structures, which do not occur in kraft pulp residual lignin, are produced as a result of the reaction between chlorine and lignin. The chemistry involving in chloroform formation from phenolic compounds has been extensively studied in connection with treatment of drinking water rather than in the context of pulp bleaching. Rook observed trihalomethanes generation when naturally colored water was treated by chlorine.[51] He characterized the precursor of chloroform as humic substances, or more appropriately fulvic acids.[52] Aromatic rings with two free meta-hydroxyl groups (resorcinols) were proposed as the chloroform precursors, since those with ortho- and para- hydroxyl groups (catechols and hydroquinones, respectively) gave little or no chloroform by hypochlorite treatment. Several researchers have verified his observation, and lots of phenolic compounds that can be chloroform precursors have been investigated.[53] More generally, the 1,3-dihydroxy structures lead to higher yields of chloroform in acidic, neutral and alkaline condition than the 1,2-dihydroxy and 1,4-dihydroxy structures. In the case of chlorine (or hypochlorite) bleaching of lignin, it is assumed that chloroform precursors are produced from chlorinated phenolic structures via 1,3-hydroxy or 1,3-diketone structures (Fig.1-4). Part of chlorine substituted on aromatic ring is attacked by OH^- (or H_2O) and eliminated to form a 1,3-hydroxy structure as an intermediate. The intermediate is further subjected to oxidation by chlorine (hypochlorite), decarboxylation and hydrolysis to form chloroform precursors. Under alkali condition, the precursors are easily hydrolyzed by the attack of OH^-, resulting in the formation of chloroform.

In chapter 4, quantitative study on the formation of chloroform will be discussed.

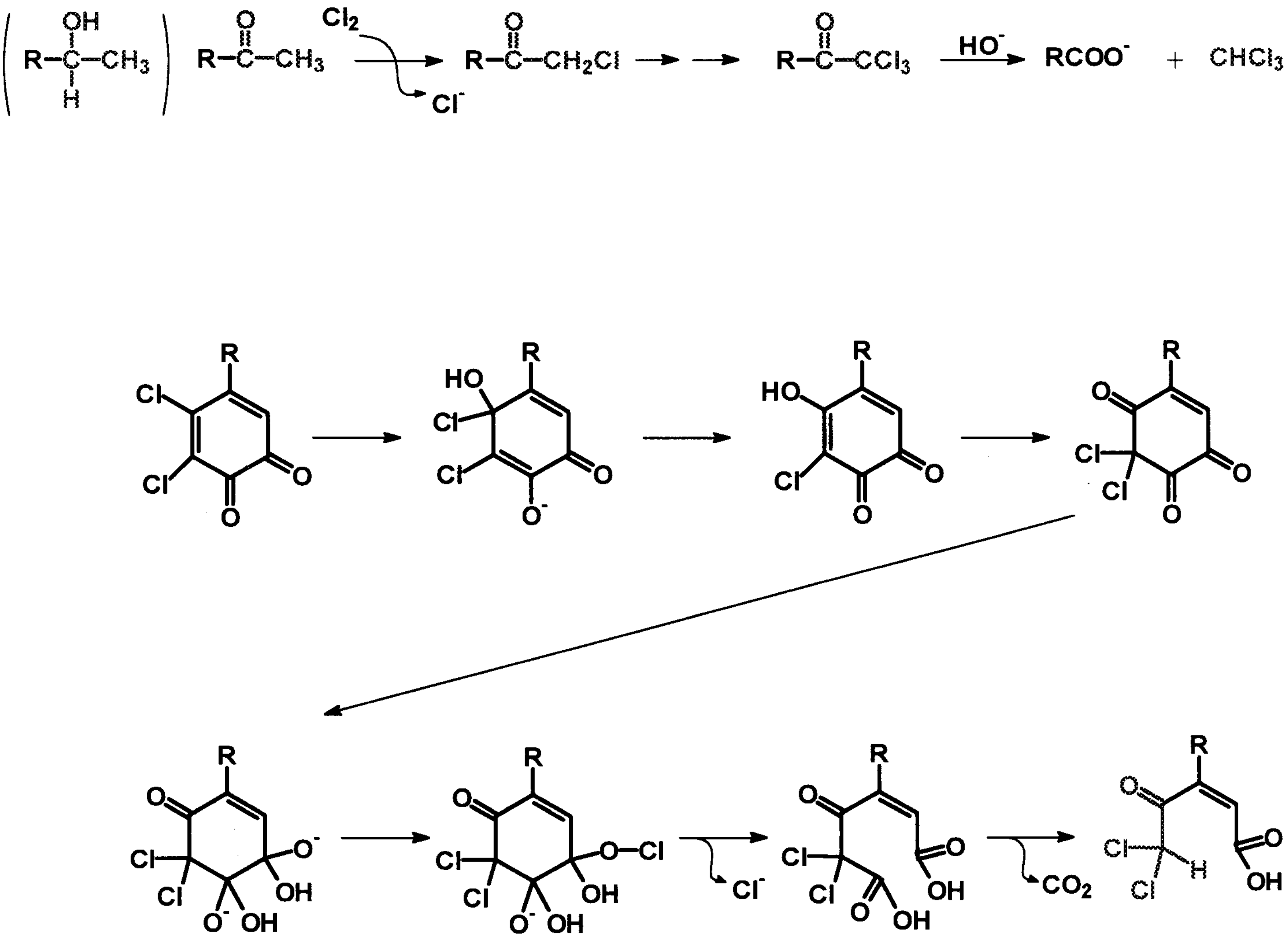


Fig. 1-4 Schematic formation mechanism of chloroform precursor from structurally modified lignin by chlorine treatment

1.3. Analytical Pyrolysis

Pyrolysis-gas chromatography (Py-GC) is an analytical procedure for the chemical structure of macromolecular substances by the use of pyrolyzer equipped with gas chromatograph. Various attempts other than Py-GC (i.e. thermogravimetry) have been made to obtain some physical and/or chemical information on the components of high molecular weight organic substances by heating them. The Py-GC is different from these conventional attempts in that Py-GC has a lot of unique advantages. Py-GC needs very small amount of sample, short period of time for analysis, and in general no pretreatment of the sample. The principle of this method, often called "analytical pyrolysis" can be summed up as follows; Samples, carrying complicated structures as a macromolecule, are degraded instantaneously by the heat under anaerobic condition. Relatively weak chemical bondings in high molecular compounds are easily cleaved spontaneously by heating under a certain controlled condition of analytical pyrolysis, to yield low molecular weight compounds from which some information about the structure of the original high molecular weight compounds can be obtained. These low molecular weight compounds are detected chromatographically. Flame ionization detector (FID) and mass spectrometric detector are frequently used as detectors.

Analitical pyrolysis sometimes gives useful information when other analytical procedures are not be applicable. It was once very difficult and challenging to keep the temperature of pyrolyzer constant when samples were heated. In recent years, new types of pyrolyzers such as microfurnace pyrolyzer and Curie-point pyrolyzer have been developed. By the Use of these pyrolyzers, samples can be heated very rapidly to the desired temperature. These pyrolyzers have greatly improved the reproducibility of temperature control. It is noteworthy that the development of GC capillary column (i.e. fused silica capillary column) helps to apply this analytical technique to the macromolecule analysis in a wide variety of research fields.

Davison, who is often referred to as a pioneer in this field, first applied this procedure to the analysis of synthetic fiber.[54] Since then Py-GC has been used for the analysis of synthetic polymer, but the application range of it was very limited. It was not until in the 1960s that Py-GC was applied to the analysis of lignin, one of the most abundant biopolymers on the earth.[55] Various chemical analyses such as nitrobenzene oxidation, methylation-potassium permanganate oxidation, acidlysis, thioacidolysis, and ozonation, combined with a variety of spectroscopic analytical tools such as IR, UV, ^{1}H-NMR, and ^{13}C-NMR are used for the analysis of lignin. Analytical pyrolysis does not basically requires pretreatment or isolation of samples which often gives rise to some modification of lignin, and is expected to be a promising tool for rapid and simple analysis of lignin preparations. Analytical pyrolysis gives a lot of pyrolysis products each with different side chain from lignin aromatics.

Kuroda *et al*,[56-64] Faix *et al*,[65-69] and other reserchers[70,71] have investigated various lignin preparations and other wood components (i.e. carbohydrates) by the use of analytical pyrolysis. Over 80 pyrolysis products have been identified so far. Loon and co-workers[72] found some chlorinated guaiacols, phenols, and low molecular weight aliphatic substances from pulp mill effluent pouring into the river Rhine nearby. Sasaki *et al*[73,74] analyzed chlorinated kraft lignin and tried to find the degradation behavior of it. But so far few attempts have been made to apply this analytical technique to the systematic analysis of high molecular weight components of pulp bleaching effluent.

Low molecular weight components of bleaching effluent is relatively easy to analyze by gas- or liquid-chromatographic procedure, and a lot of reports were published.[75-78] However, the analytical methods that are appropriate for high molecular weight components of pulp bleaching effluent have not yet been established. Analytical methods frequently used in wood chemistry (i.e. nitrobenzene oxidation [mentioned above]) to investigate aromatic structure of lignin are not applicable to the analysis of such high molecular weight compounds without pretreatment. This is because those components do not show aromatic character (aromaticity), in spite of the fact that most of them have their origin in lignin aromatics. In chapter 5, chlorinated lignin and other oxidized lignins are analyzed by Py-GC/MS and the application of this technique to modified lignins with high molecular weight is discussed.

1.4. Objectives of This Work

A variety of chloro-organics are inevitably produced in the process of degradation and/or removal of lignin, one of the major wood components, by chlorine bleaching of kraft pulp, which is now of greatly environmental concern. This is the reason non-chlorine or less-chlorine bleaching technology is being widely applied in plant-scale, especially in the West. On the other hand, chlorine bleaching is still usually employed as a main sequence in Japanese pulp and paper industry. Huge amounts of chloro-organics are produced in such a process and released to the environment. It is an urgent task to acquire a better understanding of the formation mechanism of these organic compounds. It is also of vital importance to establish an estimation procedure for the fate of these substances in the ecosystem. As for the reactivity toward lignin, chlorine is one of the most effective bleaching agents. The whole knowledge of chlorine chemistry is not fully established, especially it is not clear what is the major reaction responsible for lignin degradation and delignification during chlorine bleaching. It is important to obtain the whole knowledge of chlorine chemistry in order to clarify the basic characteristics of chloro-organics produced during chlorine bleaching, which is scientifically interesting as well. It will be of great use to establish the knowledge systematically, because the possibility to develop a new bleaching technology may also expand.

Objectives of this study are as follows;

1. To evaluate quantitatively the degree of oxidation reaction by chlorine during chlorine bleaching of kraft pulp by the determination of chloride formed in the process

(chapter 2)

2. To estimate the structural modification of lignin aromatics by the determination of methanol liberation and methoxyl content, then to discuss how it is related to the lignin removal in the chlorine bleaching process (chapter 3)
3. To determine chloroform that can be produced during chlorine bleaching of kraft pulp (chapter 4)
4. To clarify the specific structures of oxidized lignins (especially high molecular weight chloro-organics) by the application of analytical pyrolysis (Py-GC/MS) (chapter 5)

Throughout this study, significance of oxidation reaction by chlorine during chlorine bleaching will be discussed by using many analytical methods and emphasized in any chapter in this thesis.

2. Evaluation of the Extent of Oxidation Reaction during Chlorine Bleaching of Pulp

Summary: A modified method was developed to evaluate how much chlorine is consumed by oxidation reaction during chlorine bleaching process. This evaluation is, in principle, based on the sum of chloride produced during chlorination stage (C-stage) and produced during alkali treatment of both the C-stage effluent and the chlorinated pulp. Results obtained by this method proved that about 50 to 75 % of chlorine was consumed by oxidation reaction during chlorine bleaching, depending on the reaction condition of chlorination. Even under a reaction condition which is not favorable to an oxidation reaction (low pH), approximately 3 electrons were abstracted from one lignin structural unit by chlorine bleaching.

2.1. Introduction

Chlorine is a very effective bleaching agent, but it brings a serious environmental problem because it forms chloro-organics inevitably during chlorine bleaching process. Alternative bleaching agents are, therefore, being developed all over the world. It is important to know in detail how chlorine reacts with residual lignin in kraft pulp, and the knowledge would be useful for the development of new bleaching agents comparably effective to chlorine. However, the major reaction responsible for delignification during chlorine bleaching process has yet to be fully understood.

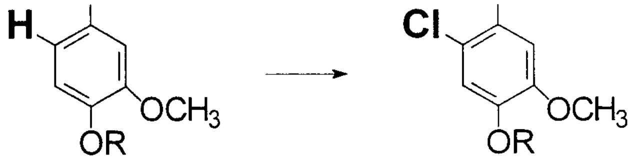
Possible reactions reported in early studies[1] are summarized in Fig.2-1. The chlorine-consuming reactions are divided mainly into two patterns: substitution and oxidation reactions expressed as equations [1] and [2], respectively. Although chlorine substitution reaction is essentially an oxidative reaction, the substitution reaction and oxidative reactions other than the substitution reactions have been historically classified into different categories in the field of bleaching chemistry. This classification has provided some fruitful results for the better understanding of chlorine bleaching. In this report, the above traditional classification was used to express the types of reaction during chlorine bleaching.

Substitution reaction consumes one mole of chlorine to form one mole of chloride, whereas oxidation reaction consumes one mole of chlorine to form two moles of chloride. Catalytic hydrolysis (eq.[4]), on the other hand, does not consume any chlorine molecule although it is assumed to be greatly related to the changes of lignin structure.

It was once supposed[2] that during chlorine bleaching substitution reaction contributed more to delignification than oxidation, and that oxidation should be

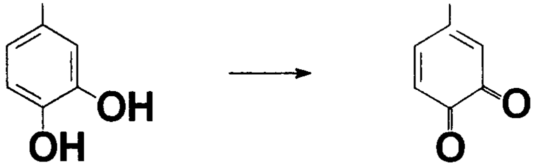
[1] substitution reaction

$$\text{R-C-H} + \text{Cl}_2 \longrightarrow \text{R-C-Cl} + \text{H}^+ + \text{Cl}^-$$



[2] oxidation reaction 1

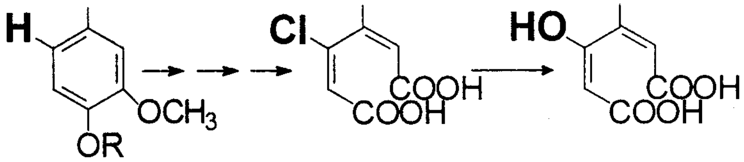
$$\text{R-CH}_2\text{-OH} + \text{Cl}_2 \longrightarrow \text{R-CH=O} + 2\text{H}^+ + 2\text{Cl}^-$$



[3] oxidation reaction 2

1) $\text{R-C-H} + \text{Cl}_2 \longrightarrow \text{R-C-Cl} + \text{H}^+ + \text{Cl}^-$

2) $\text{R-C-Cl} + \text{OH}^- \longrightarrow \text{R-C-OH} + \text{Cl}^-$



[4] catalytic hydrolysis

$$\text{R}_1\text{-O-R}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \longrightarrow \text{R}_1\text{-OH} + \text{R}_2\text{-OH} + \text{HClO} + \text{HCl}$$

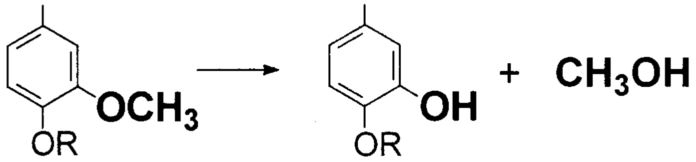


Fig. 2-1 Name of reactions which are used to express types of chlorine reaction

suppressed to maintain the strength of pulp obtained. Grangaard *et al*[3] pointed out that some chlorine consumption by oxidation reaction also play an important role in rendering the lignin in kraft pulp soluble when lignin content in pulp is relatively low. But they did not put a strong emphasis on the indispensability of oxidation because they supposed substitution reaction to be important as well. Tabei and co-workers,[4] on the contrary, suggested that the effect of oxidation reaction on delignification should be of greater importance. They observed quantitatively delignification behaviors by varying intentionally the proportion of the oxidation and the substitution reaction under a given chlorine consumption. They proposed a method how to evaluate the amount of chlorine consumed by oxidation and substitution reactions. As will be discussed in the part of results and discussion, their calculation was based on the amount of chloride determined in chlorination stage (C-stage) effluent. But the presence of structures carrying unstable organic chlorines[5] in both the C-stage effluent and the chlorinated pulp was out of consideration. Some of the structures with organically bound chlorine produced during C-stage (seen as eq.[1]) are susceptible to warm alkali treatment to form chloride (described as eq.[3]).[5] If the amount of chloride can be used as the measure of the extent of oxidation reaction, such chlorides released from organically bound chlorines during alkali treatment should also be taken into account. For example, as expressed in the eq.[3], the resulting structure carries, in most cases, a hydroxyl group at the position where a hydrogen atom was present before the chlorination reaction. Conversion of a carbon-hydrogen bond into a carbon-oxygen bond is certainly an oxidative reaction. It should be noted here that organically bound chlorines in chlorinated phenols are in most cases quite stable to such a warm alkali treatment employed in this experiment.[6] Therefore, in order to estimate properly the extent of oxidation reaction during chlorine delignification, the chloride not only produced during C-stage but also derived from such unstable organic chlorines by a warm alkali treatment must be determined. The significant role of oxidation reaction in the chlorine bleaching was evaluated in this document on the basis of a modified calculation method.

2.2. Experimental

2.2.1. Evaluation of the Extent of Oxidation Reaction

2.2.1.1. Chlorination

Unbleached hardwood kraft pulp (LUKP: kappa number 11.5, 20g on oven dry weight basis) was treated with chlorine water (chlorine multiple was 0.15 and the pulp consistency was 5%) under following two conditions. Chlorine multiple is defined as the chlorine charge in percentage (% on pulp) divided by the kappa number of unbleached pulp.

Condition 1:

treated with chlorine water prepared by the introduction of gasous chlorine into deionized water without pH adjustment (pH was found to be pH 2.5 after one hour of bleaching at room temperature)

Condition 2:

treated with pH-adjusted chlorine water prepared by the addition of NaOH to the chlorine water (pH was found to be pH 4.4 after two hours of bleaching at room temperature)

Each bleached pulp was separated from chlorination liquor and washed three times with 300 ml each of deionized water. Chloride contained in chlorination liquor and three washings was determined according to the procedure described in the section 2.2.1.3.

2.2.1.2. Alkali Treatment

Chlorination liquor and the first washing were treated separately with NaOH at 70°C for 1 hour. The NaOH doses were varied so that the molar ratio of NaOH to the amount of chloride detected in the liquor before alkali treatment ranged from one to ten. After the treatment, each sample was cooled and chloride contained in those solutions was determined.

Chlorinated pulp (1g) was also treated with NaOH solution under 70°C for 1 hour, and chloride released into suspension was determined. NaOH doses (g) employed here were 0.5, 1.0, 2.0, 5.0, and 18% of the weight of chlorinated pulp. After the treatment, each sample was cooled and chloride contained in those suspensions was determined.

2.2.1.3. Chloride Determination

Chloride in the C-stage liquors (before and after alkali treatment) and chloride released from chlorinated pulps after the alkali treatment were determined by an ion chromatography (LC-10A series: SHIMADZU) with bromide (added as 0.10 mM KBr solution) as an internal standard.[7] The determination was carried out on an anion-exchange column (Shim-pack IC-A1) with an electrical conductivity detector (CDD-6A: SHIMADZU). The eluent was tris(hydroxymethyl)aminomethane buffer (0.42mM: pH 3.5) containing 0.50mM phthalic acid. The flow rate was 1.5ml/min. Temperature of the column and detector was 40°C. Injection volume was 20μl at each operation.

2.3. Results and Discussion

2.3.1. Calculation of the Proportion of Oxidation and Substitution Reaction

The proportion of oxidation and substitution reaction during chlorine bleaching can be calculated based on the amount of chloride produced by the reaction.

[calculation]

$$\text{Substitution (\%)} = (2x - y) \times 100 \div x$$

$$\text{Oxidation (\%)} = 100 - \text{Substitution (\%)}$$

$$= (y - x) \times 100 \div x$$

〔where; x : Cl_2 consumed (mol), y: Cl^- produced (mol)〕

As the value (*y*), the method of Tabei and others[4] employed only the chloride determined in the chlorination stage (C-stage) liquor. Contrary to this, the modified method by the candidate employs total chloride ions found in C-stage liquor and produced by the alkali treatment of both C-stage liquor and chlorinated pulp. In this study, the amount of Cl_2 consumed in the C-stage was regarded as that of Cl_2 added because no residual chlorine was detected in any C-stage liquors or washings after the reaction by iodometric titration.

Fig.2-2 shows the amount of chloride determined in C-stage liquor and three washings before alkali treatment. Irrespective of the difference between the two conditions employed, almost all the chloride determined without alkali treatment was found in the C-stage liquor and the first washing, and thus it can safely be said that chloride existing in C-stage liquor and the first washing practically represents the

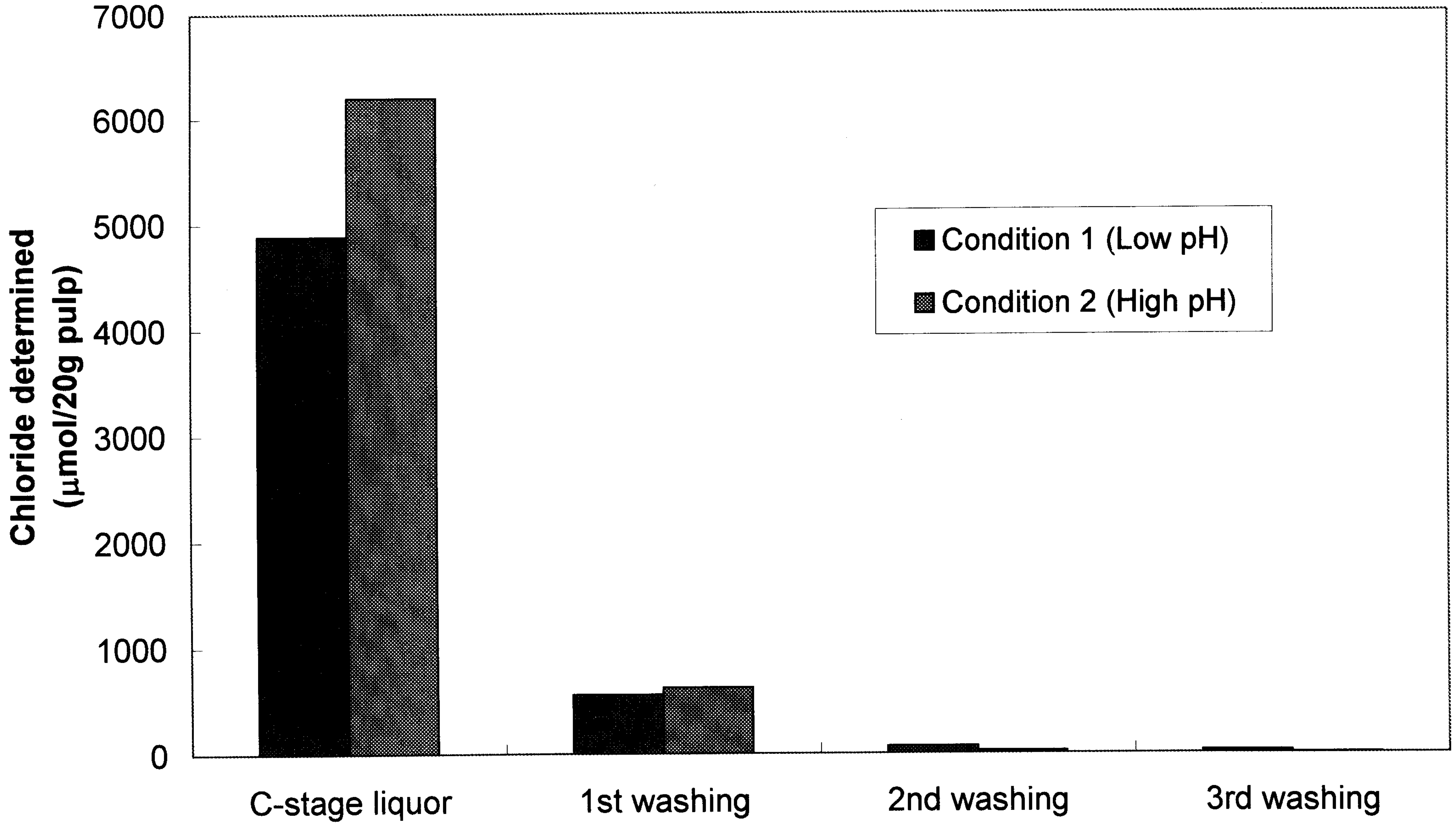


Fig. 2-2 Chloride determined in C-stage liquors and washings

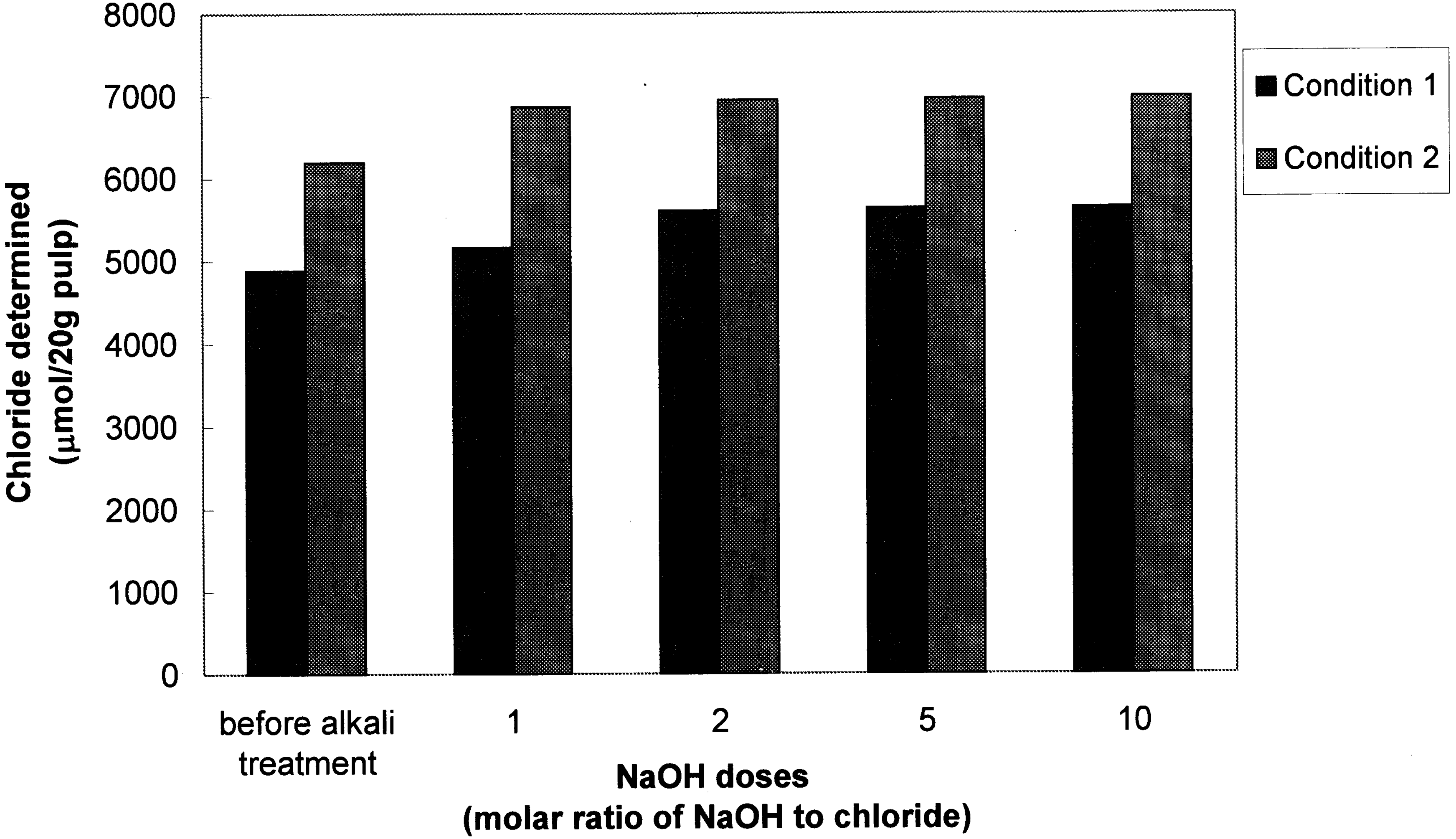


Fig. 2-3 Increase in chloride in C-stage liquor by 70℃ alkali treatment

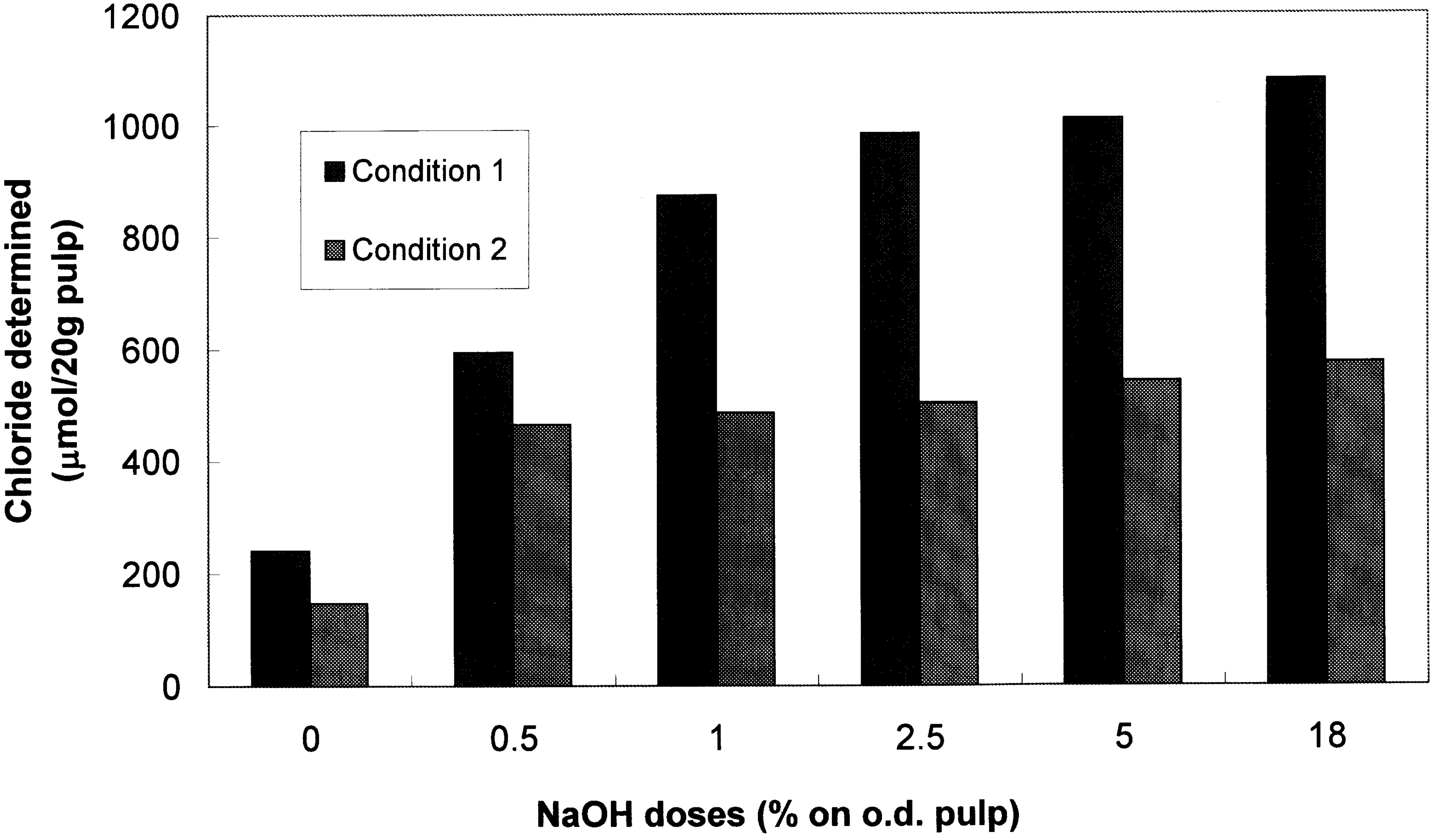


Fig. 2-4 Liberation of chloride from chlorinated pulp by 70℃ alkali treatment

chloride produced during C-stage. This amount of chloride is described as (***a***), and it will be used to evaluate the proportion of oxidation and substitution reaction according to a calculation method previously proposed by Tabei and co-workers.[4] The result will be compared with that obtained according to the modified method.

The C-stage liquor and the first washing were treated with warm alkali, and then chloride was determined again. The effect of NaOH dose on the amount of chloride found in alkali-treated C-stage liquor is shown in Fig.2-3. In both conditions 1 and 2, chloride amount increases with the increase in the NaOH dose, and finally reached a constant value at a certain level of NaOH dose. A similar tendency was observed for the first washing prepared under both conditions (data not shown). The sum of chloride determined in C-stage liquor and the first washing after NaOH treatment (NaOH dose was ten equivalent times of the chloride detected before alkali treatment) is defined as (***b***), and it will be used in the modified calculation method as discussed later.

Chlorinated pulps were also subjected to a treatment in warm NaOH solution. As shown in Fig.2-4, the amount of chloride released from the pulp increases with the increase in NaOH dose, and finally reached a constant value. A similar tendency was observed for both chlorinated pulps. Chloride measured after warm alkali treatment (NaOH 18% on pulp) is defined as (***c***), and will be used in the modified calculation method.

The proportion of oxidation and substitution reaction is calculated based on the results (Fig.2-4) described so far. The results obtained by Tabei and others' method and by the modified one are compared in Fig.2-5. In the former method, the evaluation is based only on the amount of chloride produced into C-stage liquor during chlorination. According to their method, the value (***a***) is used as (*y*) in the calculation formula described above. The results obtained by this conventional method are expressed as calculation 1 in Fig.2-5. On the other hand, the modified method developed in this study employs (*b*)+(*c*) as the value (*y*) in the calculation formula. The results obtained by the candidate's modified method are described as calculation 2 in Fig.2-5.

Obviously there is a large difference between the results obtained by two calculation methods as shown in Fig.2-5. The proportion of oxidation during chlorine bleaching should be properly estimated in order to make a first step to learn the major reaction responsible for delignification. As mentioned earlier, substitution reaction consumes one mole of chlorine to form one mole of chloride, whereas oxidation reaction consumes one mole of chlorine to form two moles of chloride. Some organically bound chlorine atoms which are labile to alkali treatment to form chloride are left out of account according to the conventional method (calculation 1). It is clear that the proportion of oxidation reaction has been extremely underestimated. The result obtained by our modified method (calculation 2) proved that when 0.15 of chlorine multiple was employed, about 50 to 75 % of chlorine was consumed by oxidation reaction during chlorine bleaching of hardwood kraft pulp, depending on the reaction condition of chlorination. We can say with fair certainty that oxidation plays a much more important role than assumed by early results.

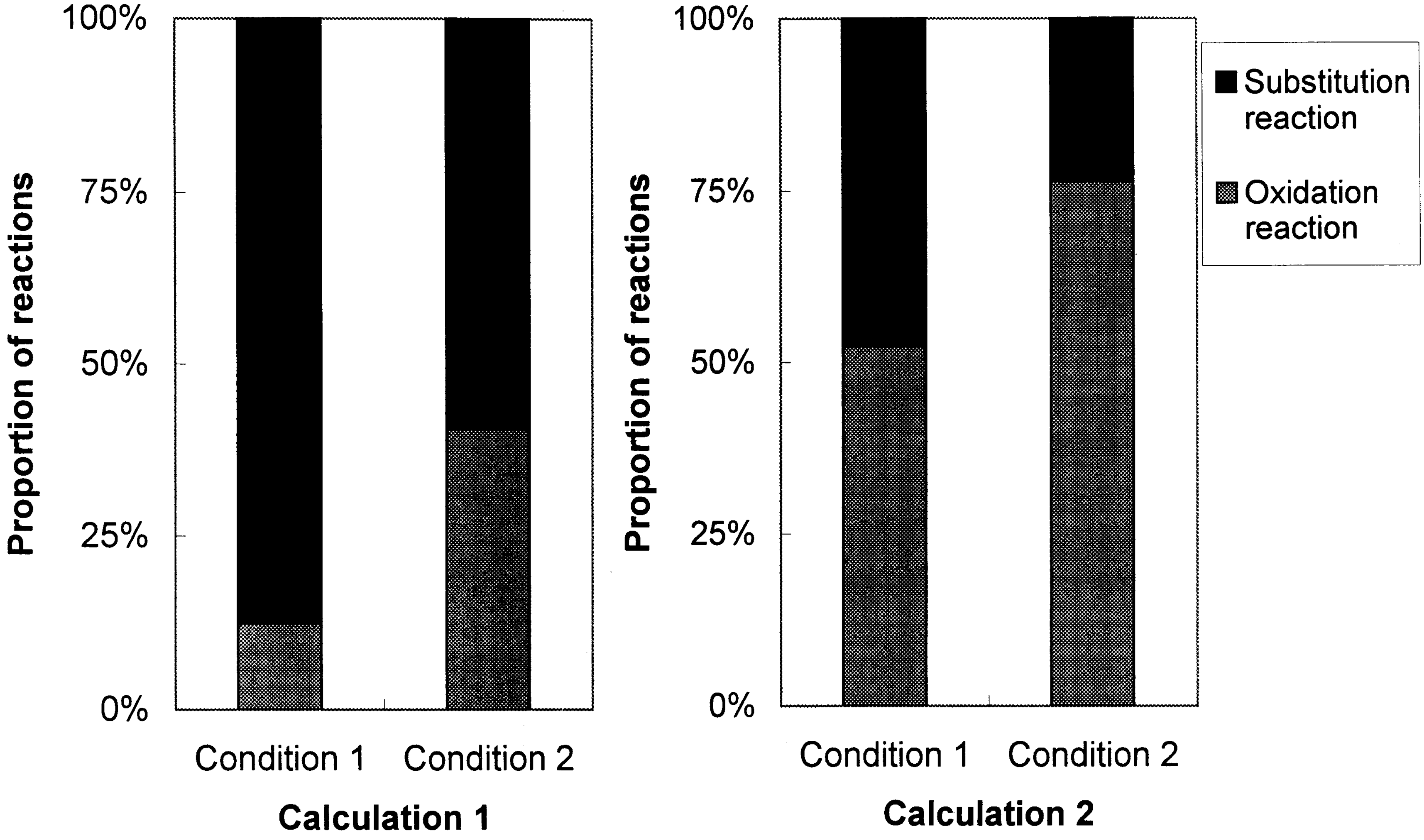


Fig. 2-5 Contribution of chlorine oxidation calculated by two methods

2.3.2. Comparative Study on Various Oxidizing Agents

On the basis of the amount of chlorine consumed by oxidation reaction (calculation 2: Fig.2-5), it is possible to calculate how many electrons were abstracted from one phenylpropane unit of lignin structure. When the equivalent molecular weight of lignin (EMW) is assumed to be 200, it was found that approximately 3.0 to 4.4 electrons were abstracted from one lignin structural unit during chlorine bleaching of hardwood kraft pulp, depending on the reaction condition of chlorination (Fig.2-6). It should be noted that no less than three electrons were abstracted from one lignin unit even under a reaction condition which is not favorable to oxidation reaction. Since four-electron-abstraction from one aromatic nucleus corresponds to a ring opening reaction, this result provides an additional evidence for the extensive oxidation during chlorine bleaching process.[8] It is surprising that 4.4 electrons were abstracted from one lignin structural unit, though the reaction was conducted under oxidation-favorable reaction condition (using pH-adjusted chlorine water) which is not applied to commercial use. Chlorine-free bleaching agents such as oxygen and hydrogen peroxide, with an exception of ozone, which are being in wide use all over the world, can never achieve that degree of oxidation. Regardless of whether it has phenolic structure or not, it is possible to degrade any lignin structural unit if a bleaching agent shows such a strong oxidizing power. It is said that compared with any chlorine-free bleaching agent, chlorine can maintain pulp strength property because it does not produce active chemical species that attacks carbohydrates. Although chlorine may bring serious environmental impact, it can be concluded that chlorine is given priority over any other bleaching agent as far as its reactivity toward lignin is concerned.

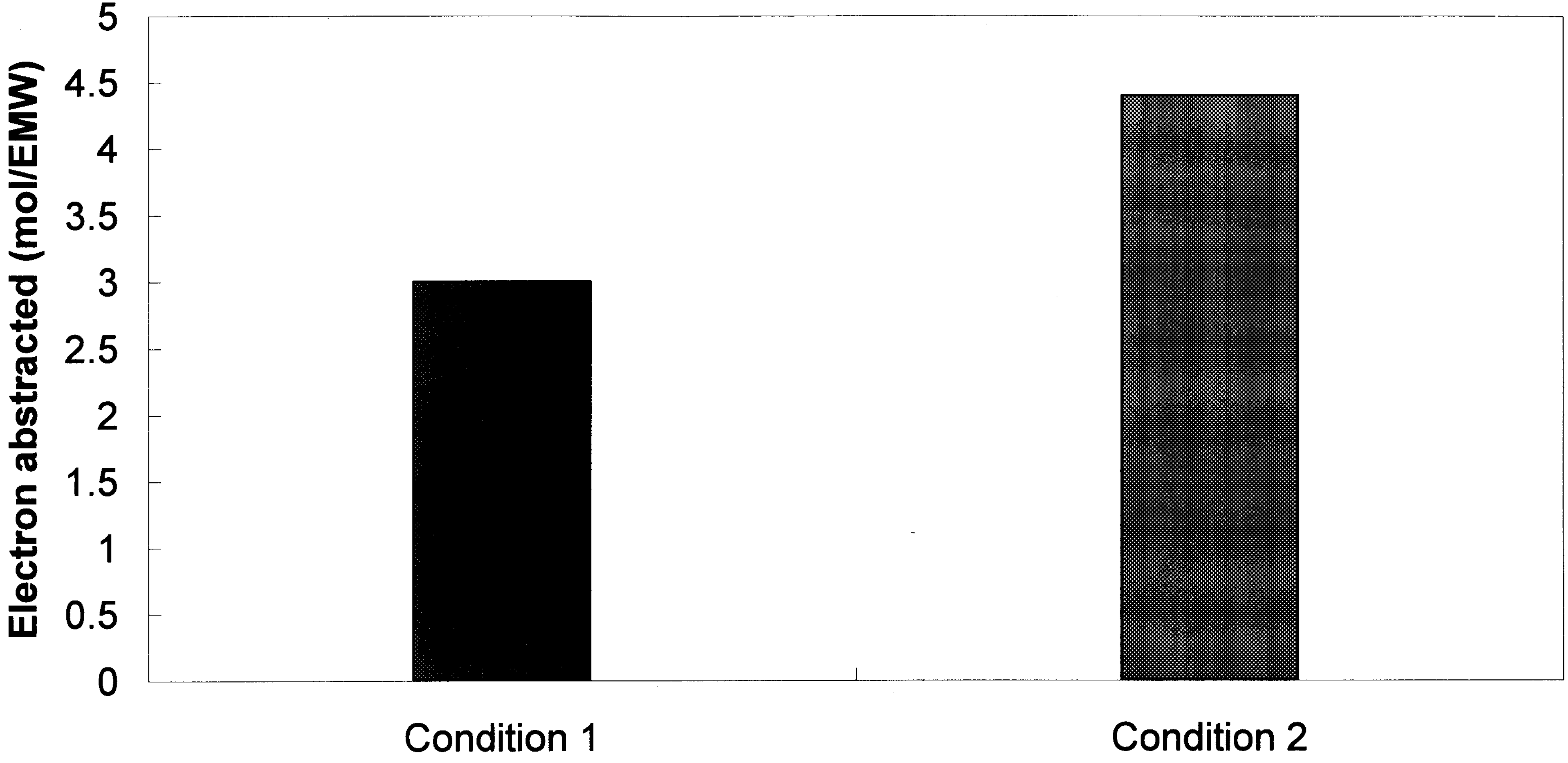


Fig. 2-6 The extent of oxidation expressed as the number of electrons abstracted from one phenylpropane unit after C- and E-stages.
EMW: equivalent molecular weight of lignin (200)

2.4. Conclusions

The candidate, focusing on the importance of oxidation reaction by chlorine, calculated the proportion of oxidation reaction and substitution reaction occurred in the course of chlorine bleaching, using pH-adjusted (high pH: oxidation-enhanced reaction condition) and pH-unadjusted (low pH: oxidation-suppressed reaction condition) chlorine waters. The calculation was based on the amount of chloride produced during both chlorination and alkali treatment of kraft pulp, which was determined by ion chromatography. The result showed that 3.0 and 4.4 electrons were lost from one lignin structural unit, depending on whether chlorine oxidation was suppressed and enhanced, respectively. This explains the importance of oxidation reaction during chlorine bleaching of pulp, which may lead to the structural modification and/or the effective removal of lignin. It is also clarified that oxidation reaction proceeds to a substantial degree even under a reaction condition (using pH-unadjusted chlorine water) where substitution reaction is thought to occur predominantly. It is strongly supported from the results that chlorine oxidation is essentially responsible for chlorine bleaching.

3. Oxidative Cleavage of Lignin Aromatics during Chlorine Bleaching of Kraft Pulp

Summary: Methanol liberation and methoxyl loss during chlorine bleaching of softwood kraft pulp were quantitatively investigated to estimate the degree of structural modification of lignin aromatics. Increase in chlorine multiple led to enhanced methoxyl loss from lignin. The result by the candidate, using pH-adjusted chlorine water (pH 5.7) with which chlorination under oxidation-favorable condition was achieved, strongly supported the importance of oxidation reaction by chlorine in delignification and lignin degradation. It was also suggested that methanol can be produced not only via catalytic hydrolysis by chlorine but via oxidative cleavage of ether bond as well. The IR spectra of chlorolignins suggested chlorine-oxidation can open aromatic rings to muconic acid derivatives without cleaving ether bonding of methoxyl group. No straight relationship between the methoxyl content and the kappa number of chlorinated pulps was obtained. Methoxyl content of bleached kraft pulps subjected to successive chlorination and alkali-extraction showed a good relationship with kappa number. This means almost all the portions of oxidatively modified lignin structure were successfully removed during these treatments while aromatic structures of residual lignin in chlorinated and alkali-extracted pulps were thought to remain intact.

3.1. Introduction

It is well known that during chlorine bleaching substantial amounts of methanol are liberated from lignin as a result of the cleavage of ether linkage between aromatic moiety and methoxyl group, which has been considered to be a catalytic hydrolysis reaction. The reaction usually called demethylation or demethoxylation reaction is assumed to be greatly involved in the structural modification of lignin, although chlorine does not lose its oxidation potential in this process (see chapter 2 in this thesis). In the previous chapter, which quantitatively estimated the proportion of oxidation and substitution reactions by chlorine by a modified method, strong emphasis was put on the important role of oxidation reaction during chlorine bleaching. In this study the progress of methanol liberation and methoxyl loss during chlorination and/or alkali-extraction was quantitatively measured in order to clarify how chlorine bleaching causes structural modification of lignin aromatics and how the structural modification of lignin is related to delignification.

First, the effect of oxidation reaction by chlorine on the progress of methoxyl removal is discussed. For this purpose, methanol liberated from methoxyl group into chlorination liquor was determined under various the reaction conditions. Then, methoxyl loss during chlorination and/or alkali-extraction stages was quantitatively determined and the relationship between methoxyl loss and the removal of lignin was discussed. These analyses make it possible to estimate what kinds of lignin are removed during C- and E-stages, and what kinds of lignin still remain after these two stages. The importance of oxidation reaction for chlorine delignification is discussed.

3.2. Experimental

3.2.1. Determination of Methanol Liberated during Chlorination Stage

Unbleached softwood kraft pulp (NUKP: kappa number 24.9, 2.5g on o.d. weight basis) was treated with chlorine water (chlorine multiple 0.01-0.50, pulp consistency 2.78%) under following two conditions (the definition of chlorine multiple is shown in chapter 2);

Condition 1: treated with chlorine water (about pH 1.7 before bleaching) prepared by the introduction of gaseous chlorine into deionized water without pH adjustment (Low pH)

Condition 2: treated with pH-adjusted chlorine water (about pH 5.4 before bleaching) prepared by the introduction of gaseous chlorine into a dilute NaOH solution (High pH)

The chlorination reaction was performed in a 50ml vial sealed with a screw cap for 60min at room temperature. Just after the addition of chlorine water, each sample was sealed and shaken for 10sec. It was shaken continually at every 10min until the end of the reaction. After the reaction, each sample was cooled in an ice bath for 10min to suppress the vaporization of methanol during pH measurement. After quick pH determination, each sample was sealed and cooled again in an ice bath for 30min. Excessive amount of reducing agent (10ml of 1M $Na_2S_2O_3$ solution) was then added to reduce residual Cl_2, if any, in the sample. Each sample was sealed and stored in a cold room (4°C) until use. From each sample, an aliquot of the suspension was transferred to a 1.5ml conical centrifuge tube, sealed with a stopper and centrifuged at 12000rpm

(10500G) for 10min at 5°C. The supernatant (1ml) was used for the determination of methanol liberated during chlorine bleaching.

The methanol determination was performed using gas chromatography (GC-8A: SHIMADZU) with FID as a detector. Packed column (2.6mm × 2.0m) coated with PEG 6000 (10%) on Shimalite TPA (60-80 mesh) was used. Column temperature was kept constant at 90°C. Injection temperature was 180°C. Detector temperature was 200°C. Helium was used as both carrier gas (pressure: 170kPa) and make-up gas (pressure: 170kPa), respectively. The gas pressures of hydrogen and air were both set at 60kPa. Calibration curve for the determination was obtained from the relationship between peak area and methanol injected, by the use of the aqueous methanol solutions with various methanol concentration. Injection volume was 20μl. Determination for each sample was performed in triplicate.

In a separate experiment, chlorination of softwood kraft pulp was performed by the same way other than it was performed in a plastic bag to determine kappa number of chlorinated pulps. The kappa number was measured according to TAPPI useful method (UM 246).

3.2.2. Preparation of Chlorolignins for the Measurement of IR Spectrum

Unbleached softwood kraft pulp (NUKP: kappa number 24.9, 9g on o.d. weight basis) was treated with chlorine water under following three conditions;

Condition 1: treated with chlorine water (about pH 1.7 before bleaching) prepared by the introduction of gaseous chlorine into deionized water without pH adjustment (Low pH)

Condition 2: treated with pH-adjusted chlorine water (about pH 5.3 before bleaching) prepared by the addition of NaOH to the chlorine water (High pH)

Condition 3: treated with non-aqueous chlorine solution prepared by the introduction of gaseous chlorine into glacial acetic acid

The reaction was performed in a plastic bag at room temperature for 60min. Chlorine multiple used was set at 0.15 at the pulp consistency of 5%.

After the treatment, each chlorinated pulp was washed three times with 180ml each of deionized water. Chlorolignin was extracted under room temperature from the chlorinated and water-washed pulp by soaking the pulp three times with 180ml of aqueous dioxane (53%) according to the procedure by Shintani *et al.*[1] Extracted chlorolignin was recovered by lyophilization.

Chlorolignin (28mg) extracted from the chlorinated pulp prepared under condition 1 was treated with a 11.2ml of NaOH solution containing 28mg NaOH. The treatment was performed in a water bath at 70°C for 60min. The whole solution was dialyzed against hydrochloric acid solution (pH 1) for 24 hours, by the use of cellulose tube

(Viskase Sales Corp.; cut off molecular weight 12000-14000). Then, the whole solution was concentrated and lyophilized to obtain alkali-treated chlorolignin.

IR spectra of chlorolignins were recorded by KBr pellet method.

3.2.3. Determination of Methoxyl Content of Pulps

Unbleached softwood kraft pulp (NUKP: kappa number 24.0, 10g on o.d. weight basis) was treated with chlorine water (chlorine multiple 0.05-0.20, pulp consistency 5%) in a plastic bag for 60min under following two conditions;

Condition 1: treated with chlorine water (about pH 1.7 before bleaching) prepared by the introduction of gaseous chlorine into deionized water without pH adjustment (Low pH)

Condition 2: treated with pH-adjusted chlorine water (about pH 5.7 before bleaching) prepared by the introduction of gaseous chlorine into dilute NaOH solution (High pH)

After the reaction, chlorinated pulp was separated from chlorination liquor by filtration and washed three times with 200ml each of deionized water. Part of chlorinated pulp (approximately 5g on o.d. weight basis) was subjected to warm alkali treatment (at 70°C) for 60min of 2.5% NaOH charge on pulp. Chlorinated pulps (CW-NKP), and successively chlorinated and alkali-treated pulps (CE-NKP) thus prepared were subjected to the determination of methoxyl content.

Methoxyl content of pulps was determined basically according to the procedure by Sporek and Danki.[2] Pulp (270mg-2.0g on o.d. weight basis) was placed in a 50ml round-bottomed flask and 57% hydrogen iodide solution (10ml) was added. A condenser was attached to the flask and methoxyl group in kraft pulp residual lignin was converted to methyl iodide under reflux at 135°C for 20min. The sample was cooled in an ice water bath after the reaction, and deionized water (10ml) and carbon tetrachloride (10ml) were sequentially added to the sample. The sample was centrifuged at 4500rpm (2800G) at 0°C for 5min to achieve complete separation of CCl_4 layer from water layer. Anhydrous sodium sulfate was then added to the CCl_4 layer and methyl iodide in the CCl_4 layer was determined by GC. Ethyl vanillin (3-ethoxy-4-hydroxybenzaldehyde: 10mg) was added to in situ generate ethyl iodide which was used as an internal standard. Calibration curve was obtained from the GC peak area ratio of methyl iodide to ethyl iodide, using varying amounts (0.8-20mg) of vanillin as a lignin model compound. Pulps were sampled so that lignin content (estimated by kappa number) was approximately 10mg.

Determination of methoxyl content was performed using gas chromatography (GC-14B: SHIMADZU) with FID as a detector. Pola PLOT Q (GL Science: 0.53mm × 25m, df=20μm) was used as a capillary column. Column temperature was kept at 120°C for 12min, raised at 5°C/min to reach 180°C, and then held at the temperature for 10min. Injection temperature was 120℃. Detector temperature was 180℃. Helium was used as both carrier gas (pressure: 75KPa) and make-up gas (pressure: 110 KPa). The gas pressures of hydrogen and air were set at 50KPa and 70KPa, respectively. Injection volume was 1.0μl. Determination for each sample was performed in duplicate.

3.3. Results and Discussion

3.3.1. Progress of Methanol Liberation during Chlorination Stage

It is well known that during chlorine bleaching substantial amounts of methanol are liberated from lignin as a result of the cleavage of ether linkage of methoxyl groups.

Reserch group of Hibbert[3] proposed that introduction of chlorine into aromatic nuclei renders aromatic methyl ethers unstable and that they become susceptible to the oxidative degradation subsequently caused by chlorine. On the contrary, Sarkanen and Strauss[4] concluded later that chlorine substitution at the ortho position to methoxyl group suppresses demethylation reaction. As a mechanism of demethylation reaction, Ivancic and Rydholm[5] suggested a kind of acid-catalyzed hydrolysis, and Sarkanen and Strauss[4] proposed a chlorine-catalyzed hydrolysis mechanism. Ni and co-workers[6] assumed that all the methoxyl groups removed from kraft pulp during chlorine treatment are converted to methanol and they concluded that all dissolved lignin fragments in chlorination liquor are demethylated. Based on this assumption, they implied that it is possible to estimate the degree of methoxyl loss as methanol in the chlorination effluent. They also reported a linear relationship between demethylation and delignification during chlorination stage, and suggested that residual lignin in chlorinated and water-washed softwood kraft pulp (CW-NKP) is not demethylated. They proposed the "methanol number" to determine lignin content of CW-NKP quickly as an alternative to kappa number determination.[7]

In order to evaluate how chlorination conditions (pH and chlorine multiple) affect the methanol liberation, chlorination of pulp was conducted by varying the chlorine multiple under two different pH conditions (Condition 1; Low pH, Condition 2; High

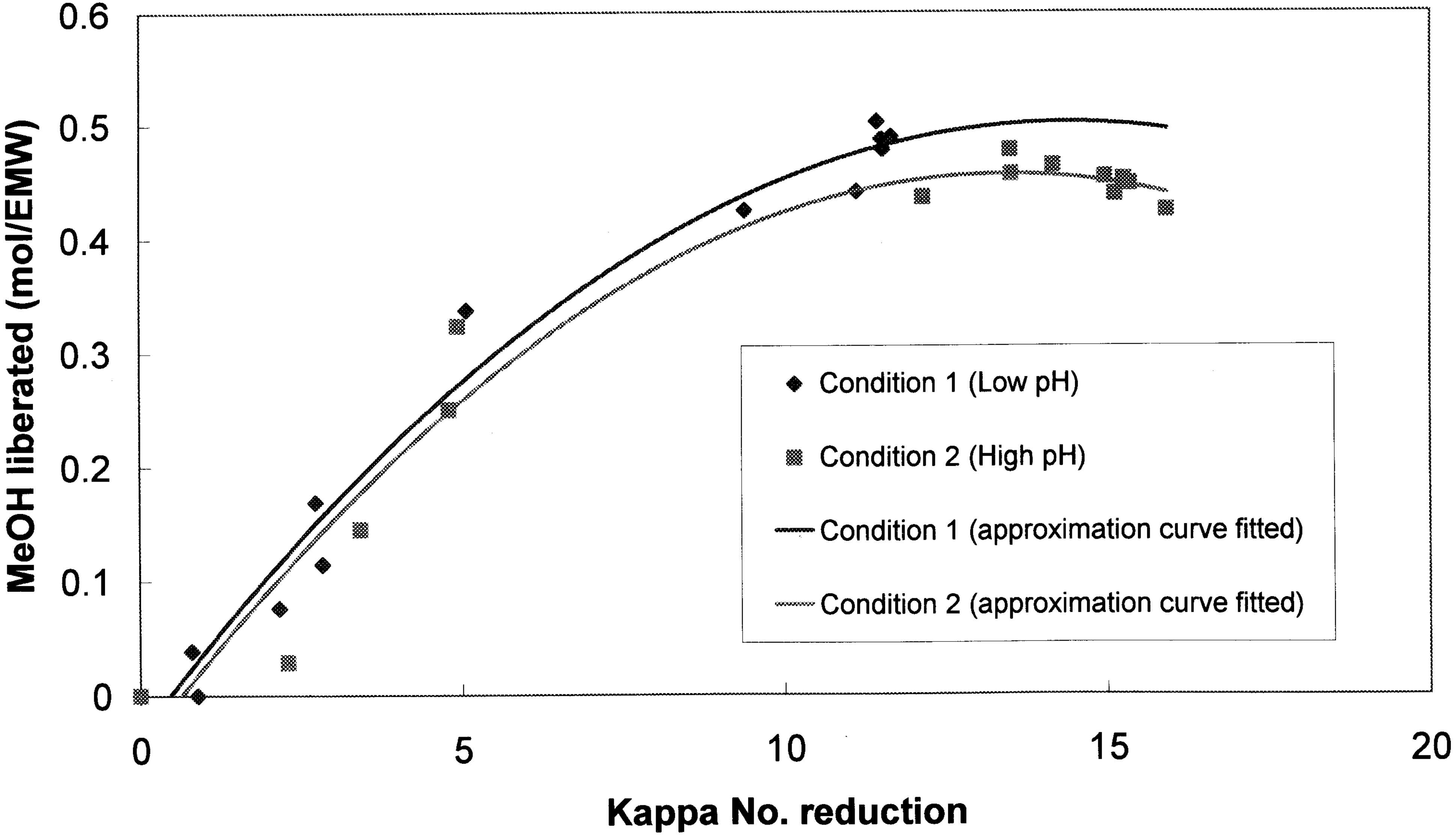


Fig. 3-1 Relationship between methanol liberation and kappa number reduction

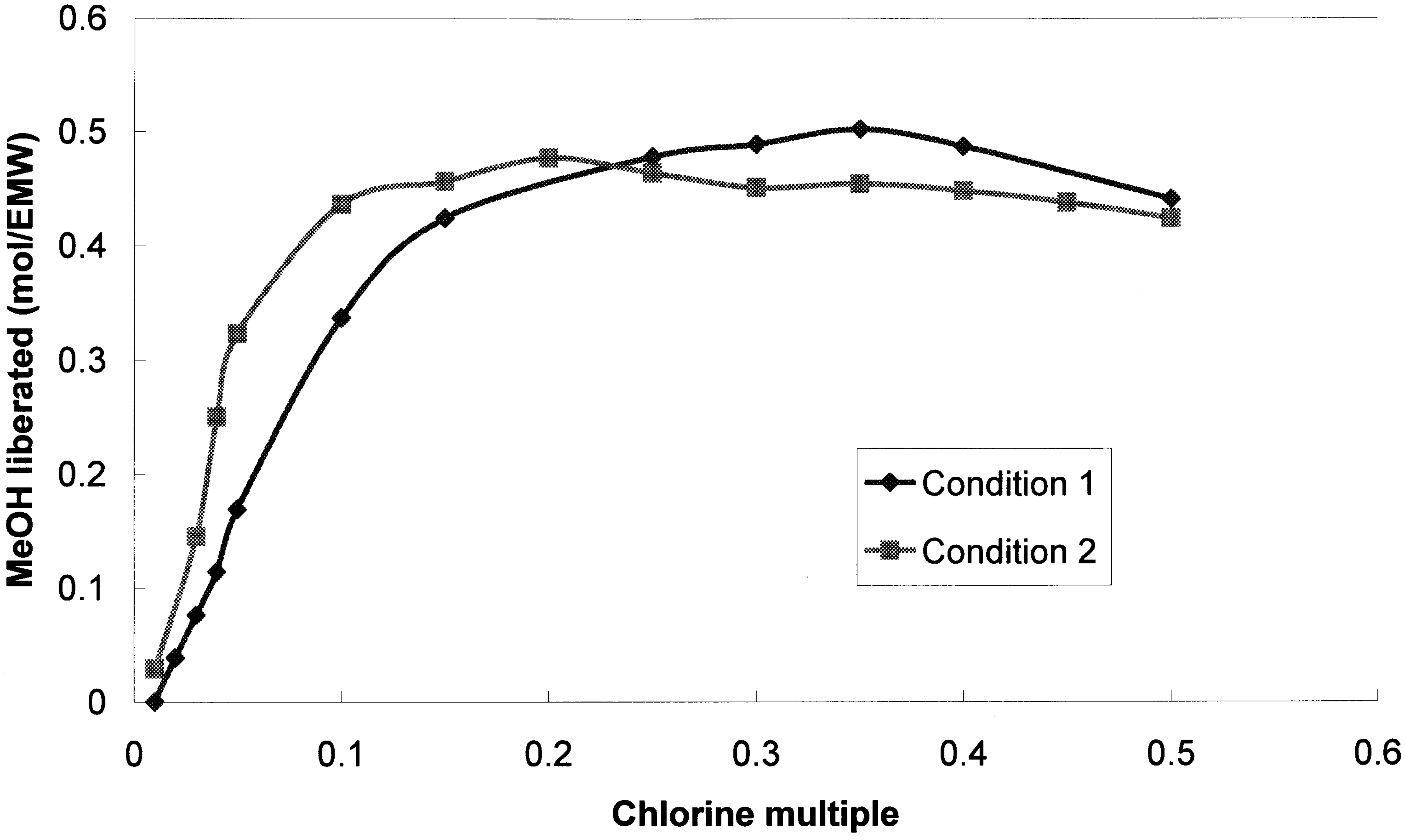


Fig. 3-2 Methanol liberation at varying chlorine multiples

pH). Shown in Fig.3-1 is the methanol liberation plotted against kappa number reduction of CW-pulp. Compared to condition 1, condition 2 was intentionally programmed so that oxidation reaction by chlorine (as HClO form) is dominant and substitution reaction is suppressed due to its higher pH value. No significant difference is observed between the conditions 1 and 2, even though methanol formation under condition 2 always appears to be slightly lower than that under condition 1. Methanol liberation seems proportional to kappa number reduction at low chlorine multiples, but no single straight line was fitted to cover all the data points from low to high chlorine multiples. This seems contradictory to the result by Ni *et al*[6] who proposed that the decrease in lignin content of CW-NKP can be determined by the measurement of methanol liberated during C-stage. Because the definition of their "chlorine free lignin" content is different from that measured by kappa number method the candidate used, it is not adequate to compare their proposal and the candidate's present results. The results by the candidate, however, revealed that the kappa number reduction of CW-NKP can not be simply expressed by the amount of methanol liberated during C-stage. In spite of such a contradictory, their results and the candidate's both demonstrated that a certain decrease in kappa number of CW-NKP was accompanied by a certain level of methanol liberation during C-stage regardless of the chlorination condition.

There was an apparent difference in the methanol liberation at a certain dose of chlorine between conditions 1 and 2 (Fig.3-2). In both conditions, methanol yields increased with chlorine multiple until about 3mg of methanol was liberated from 1g of unbleached pulp, which corresponded to approximately 0.5mol per lignin unit based on the assumption that an equivalent molecular weight (EMW) of 200 was applied. A slight decrease in methanol after the maximum value is reasonably ascribed to methanol oxidation by excess chlorine.[4] A remarkable difference can be observed between conditions 1 and 2 at chlorine multiples lower than 0.2. When chlorine multiple ranged from 0.01 to 0.2, methanol formation under condition 2 was higher than that under condition 1. The result apparently indicates that high pH is more favorable to demethylation reaction than low pH, and this seems contradictory to the previous report by White and co-workers,[3] who found that, on the basis of chlorination of soda lignin under wide range of pH, the value of methoxyl loss from lignin per chlorine consumption decreases in a order of pH 2, 6 and 10. The reason for this discrepancy is unknown at the present, but it should be noted that their results were obtained based on the methoxyl content of the recovered lignin after chlorination and that the candidate's experiment determined all the methanol liberated from methoxyl group during chlorination. If the recovery of extensively demethylated part of lignin is quite low, methoxyl content of recovered lignin can not give a proper indication for the extent of demethylation reaction.

Under condition 1 (Fig.3-2), it is reasonable to suppose that chlorine is effectively consumed by substitution reaction at low chlorine multiples, and thus, its contribution to demethylation reaction is suppressed during the early stage of chlorine bleaching. The candidate's result is in good agreement with an observation by Hosoya[8] and Hosoya *et al*,[9] who found that, by a chlorination of a β-O-4 type lignin model compound in aqueous dioxane (50%), aromatic substitution reaction by chlorine exclusively occurred during the early stage of the reaction and, after the chlorine substitution reached a certain level, demethylation reaction then started.

As a methoxyl removal, in addition to two proposed mechanism mentioned above, it is adequate to point out another possible explanation that large part of chlorine, which is present as hypochlorous acid under condition 2, enhances methoxyl loss as a result of

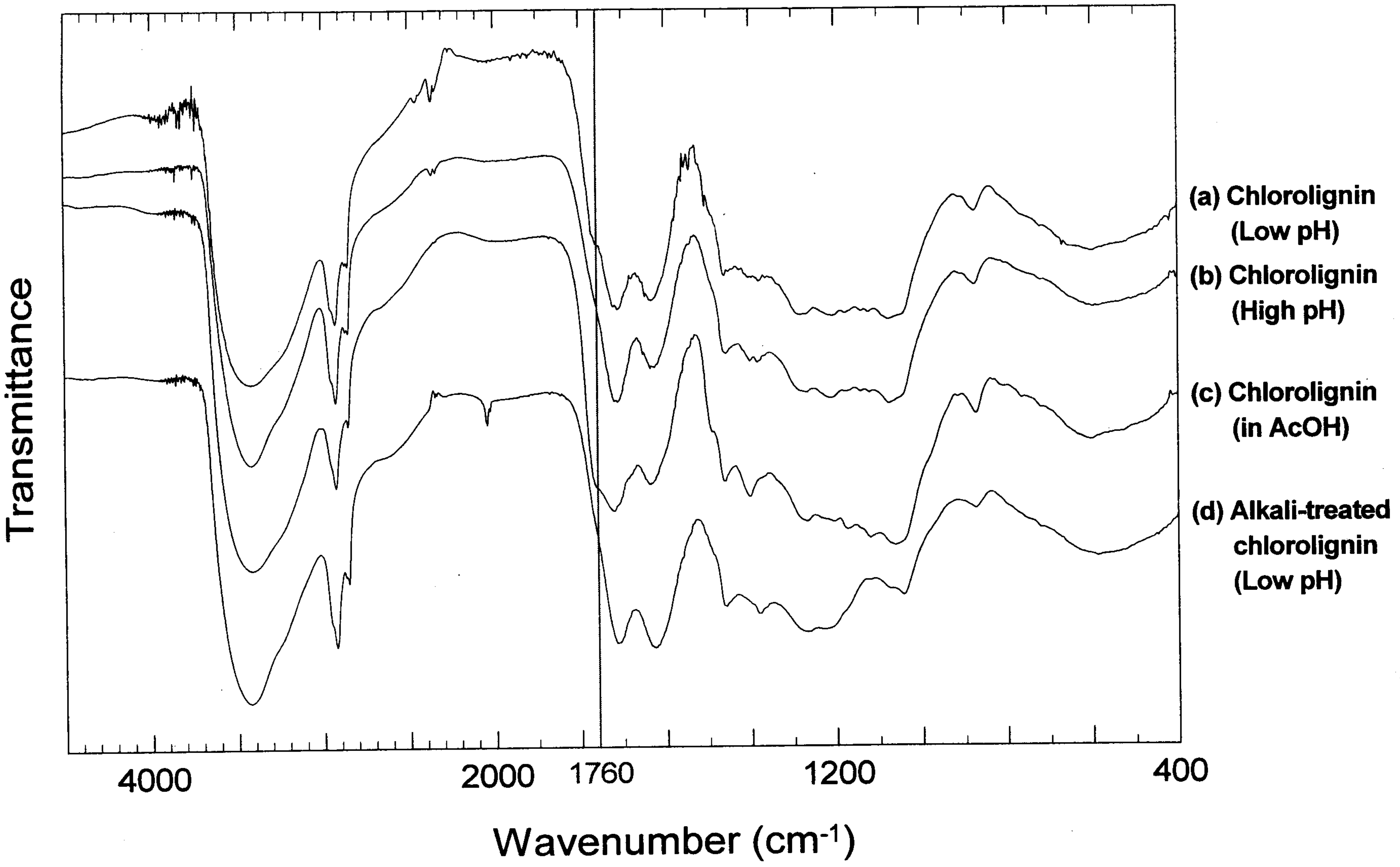


Fig. 3-3 IR spectra of chlorolignins

oxidative cleavage of aromatic moiety. IR spectra of isolated chlorolignins (Fig.3-3) seem to confirm this possibility. In all spectra, peaks in the vicinity of 1600, 1505 and 1460cm^{-1} are not seen at all, although usually they are typically found in lignin preparations due to the absorption ascribable to lignin aromatics. This suggests that a dioxane-extracted part of residual lignin in CW-pulp is so greatly modified by oxidation that aromatic character of lignin is already lost. This result strongly supports the previous result by the candidate (as described in chapter 2) and the study by Shintani and co-workers.[10] Instead of these peaks, strong peaks due to carboxylic acids are observed (1620cm^{-1} for ionized-form carboxylic acids, 1730cm^{-1} for free-form carboxylic acids). Careful attention should be paid to a shoulder absorption (1760cm^{-1}) characteristically found near a large peak. This shoulder was observed in a sample obtained from the pulp prepared in condition 1 but not in a sample prepared under condition 2. The shoulder can also be clearly seen for the sample prepared by chlorination in glacial acetic acid (condition 3: Fig.3-3), where oxidation reaction by chlorine was intentionally suppressed to a greater degree than under conditions 1 and 2. Therefore, it seemed likely that this shoulder appears only in samples where chlorination was carried out under sufficiently acidic condition. When the chlorolignin underwent warm alkali treatment, the shoulder was found to disappear (Fig.3-3, (d)) and the formation of methanol was observed, even though quantitative analysis was not performed. Thus it is thought that the shoulder can be attributed to some esters or lactones, which in general exhibit strong absorption in the range of 1700-1800cm^{-1}. This observation suggests that oxidative cleavage of aromatic part proceeds with the release of methoxyl group as methanol under condition 2 (High pH), while oxidative cleavage of aromatic part proceeds with a part of methoxyl group still remaining as ester form when chlorinated under condition 1 (Low pH).

3.3.2. Methoxyl Loss during Chlorination Stage and Alkali-Extraction Stages

In the previous section, it was demonstrated that formation of methanol was dependent on the chlorination condition (pH and chlorine multiple). It suggests that difference in chlorination condition affect the extent of modification of lignin aromatics. However, it is still not clear how the chlorination condition affects the progress of delignification. In this section, we tried to evaluate quantitatively the role of oxidation reaction of lignin aromatics in delignification during C- and E-stages.

When lignin aromatics are oxidized, in most cases methanol is released from methoxyl group, especially when the oxidation is performed under alkali condition or when it was followed by an alkali treatment. On the other hand, lignin whose aromatics are oxidized to some extent still consumes permanganate although to a lesser extent than unoxidized lignin. Therefore, the ratio of "methoxyl content / Kappa number" of a certain pulp can be used as an indication of the degree of oxidation which the residual lignin in the pulp underwent. For example, after some oxidative delignification, if this ratio of delignified pulp is smaller than that of unoxidized pulp, it can be reasonably assumed that some oxidized lignin still remains in the delignified pulp. Contrary to the above, if this ratio is the same as that of unoxidized pulp, it can be concluded that only unoxidized lignin remains in the pulp after the delignification. This method was used successfully to evaluate the extent of oxidation of the residual lignin in oxygen-bleached pulp by Tong *et al.*[11]

In the present study, the same method was applied to evaluate the degree of structural modification of the aromatic part of residual lignin in CW- and CE-NKPs. Methoxyl content of pulps are plotted against their kappa number under condition 1 (Fig.3-4) and condition 2 (Fig.3-5). Under the both conditions, the relationships between methoxyl

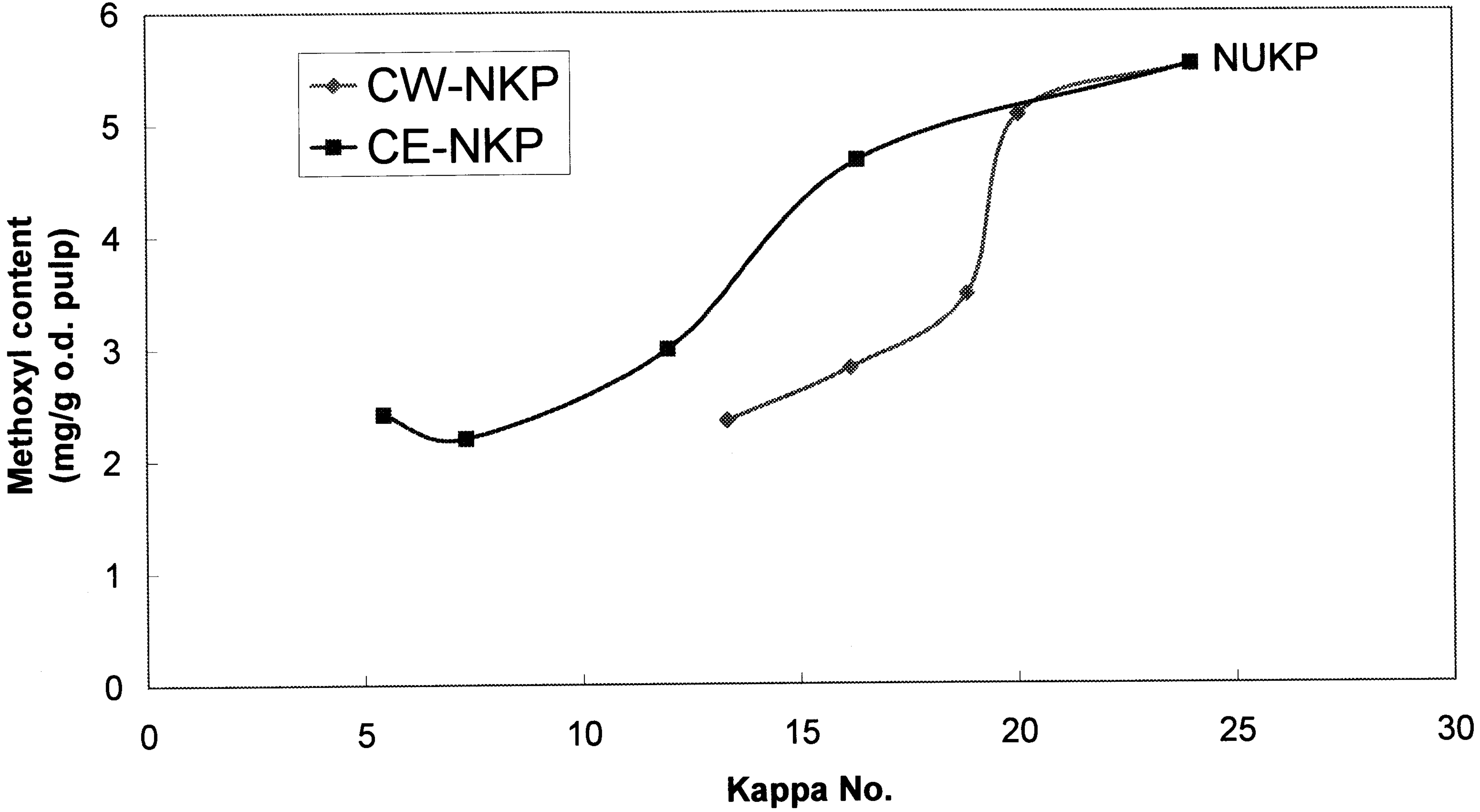


Fig. 3-4 Methoxyl content of CW- and CE-NKPs prepared under condition 1 (Low pH)

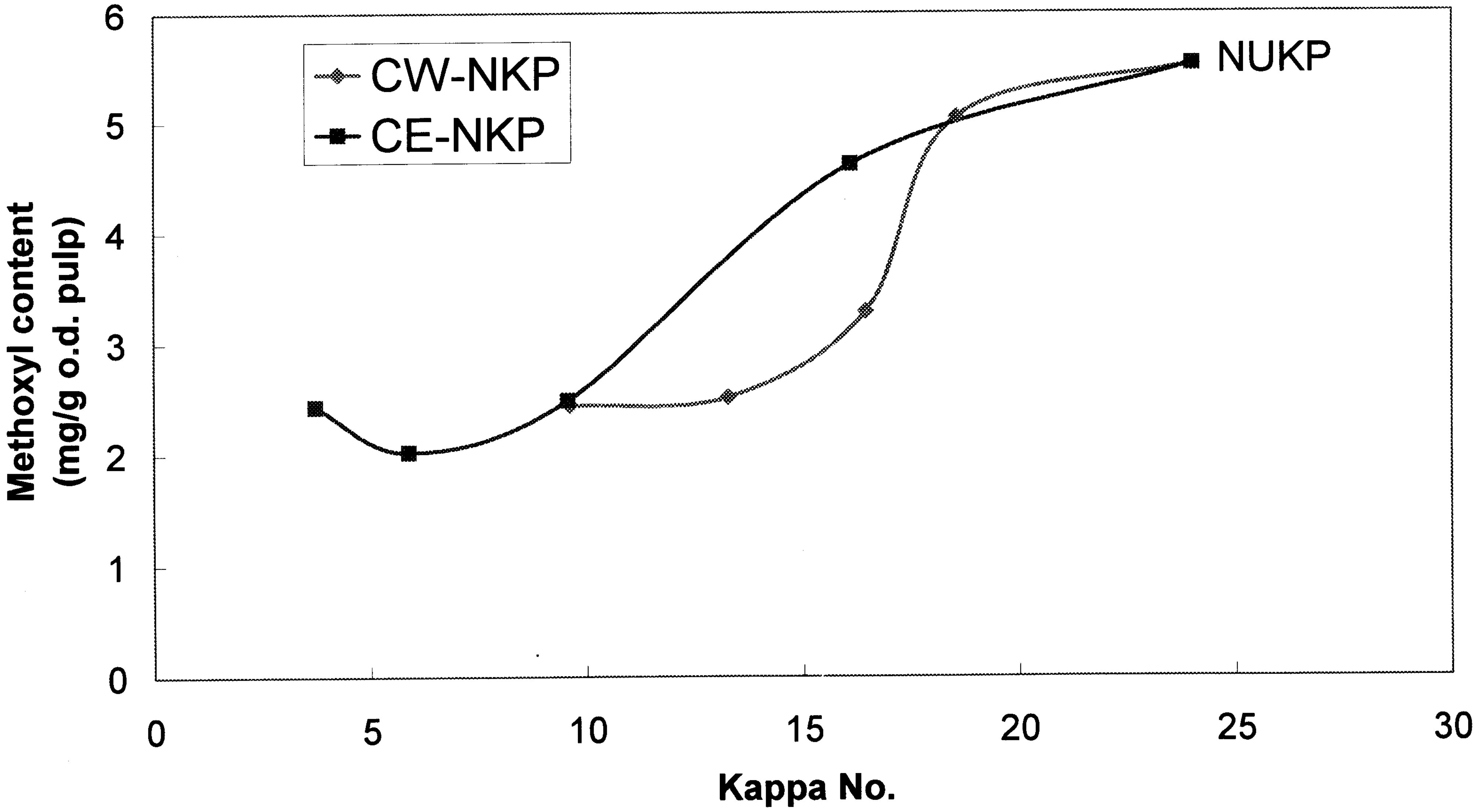


Fig. 3-5 Methoxyl content of CW- and CE-NKPs prepared under condition 2 (High pH)

Table 3-1 The calculated ratio of "methoxyl content / kappa number"

Sample ID	Chlorination Condition	Chlorine Multiple	Kappa No.	Methoxyl (mg/g pulp)	Methoxyl/Kappa
NUKP	–	–	24.0	5.5	**0.23**
CW-NKP	Condition 1 (Low pH)	0.05	20.0	5.1	**0.25**
		0.10	18.8	3.5	**0.18**
		0.15	16.2	2.8	**0.17**
		0.20	13.3	2.4	**0.18**
CE-NKP	Condition 1 (Low pH)	0.05	16.3	4.7	**0.29**
		0.10	12.0	3.0	**0.25**
		0.15	7.3	2.2	**0.30**
		0.20	5.5	2.4	**0.44**
CW-NKP	Condition 2 (High pH)	0.05	18.6	5.0	**0.27**
		0.10	16.5	3.3	**0.20**
		0.15	13.3	2.5	**0.19**
		0.20	9.6	2.4	**0.25**
CE-NKP	Condition 2 (High pH)	0.05	16.1	4.6	**0.29**
		0.10	9.6	2.5	**0.26**
		0.15	5.9	2.0	**0.34**
		0.20	3.7	2.4	**0.65**
ideal (a)	–	–	**24**	**5.6**	**0.23**

(a): hypothetically calculated value based on the assumption: 200g of lignin in pulp (Kappa number 24) carries one mole of methoxyl group content and kappa number of CW-NKP can not be expressed by a linear line, which somehow contradicts the report by Ni and co-workers[6] who proposed a good relationship between methoxyl removal and delignification after chlorination of pulp (CW-NKP). Similar contradiction is already seen for methanol liberation, as discussed in the section 3.3.1. It should be noted that the methoxyl content of the pulp does not significantly decrease before and after the alkali extraction. The ratio "methoxyl content / kappa number" of CE-NKP is higher than that of unbleached pulp. This may suggest that CE-NKP have no permanganate-consuming substances except residual lignin, while NUKP carries certain substances other than lignin that consumes permanganate (i.e. hexeneuronic acid). On the other hand, this ratio of CW-NKP was always lower than those of CE-NKP and unbleached pulp (Table 1).

It can be postulated based on the above results that delignification during C- and E-stages would proceed as following; During C-stage, extensive modification of lignin aromatics which results in the release of methanol occurs but some parts of those modified lignin aromatics still remain in pulp. Those are, however, effectively removed by alkali extraction and only unmodified lignin remains in CE-NKP. A significant difference between condition 1 (Low pH) and condition 2 (High pH) shows that the ratio (methoxyl content / kappa number) of CW-NKP prepared under condition 1 is lower than that prepared under condition 2 when they are compared at the same kappa number. This indicates that structural modification of aromatics under condition 2 causes the removal of lignin more effectively than that under condition 1. Kappa number of both CW- and CE-NKPs by a certain chlorine dose was always lower for condition 2 than condition 1 (Table 1). Since the condition 2 (High pH) is more favorable to oxidation reaction, these results again confirm the importance of oxidation reaction for chlorine delignification.

3.4. Conclusions

The effect of chlorination condition (pH and chlorine multiple) on the structural modification of lignin aromatics and on the efficiency of delignification was analyzed. Chlorination conducted under higher pH enhances the release of methoxyl group as methanol more effectively, and furthermore, resulted in more effective delignification. By analyses of the ratio between methoxyl content and Kappa number of chlorinated (CW-) and alkali-extracted (CE-) softwood kraft pulps (NKPs) suggested that aromatic moiety of residual lignin still remaining in CE-NKP was structurally unmodified. It is strongly supported again that oxidation reaction by chlorine is a key to lignin structural modification which can lead to effective delignification.

4. Quantitative Study on the Possible Formation of Chloroform during Chlorine Bleaching of Kraft Pulp

Summary: Chloroform produced during chlorine bleaching of softwood kraft pulp was quantitatively analyzed by headspace gas chromatography/mass spectrometry with single ion monitoring. Chloroform that can potentially be formed was quantitatively estimated. Chlorination and alkali treatment of pulp was performed in a gas-tight reaction vessel in order to determine chloroform as accurately as possible. By subjecting both chlorinated pulp and chlorination liquor to alkali treatment, chloroform precursors were successfully estimated. No significant effect of oxygen prebleaching on the reduction in chloroform formation per kappa number was observed. Chlorination and alkali-treatment of softwood milled wood lignin (MWL of Japanese red pine: *Pinus densiflora*) suggested a given amount of lignin, if treated at a given chlorine charge, can produce almost the same order of magnitude of chloroform as produced from unbleached kraft pulp containing the corresponding amount of lignin. The result, using pH-adjusted chlorine water (pH 5.7) by which chlorination under oxidation-favorable condition was achieved, showed the large contribution of oxidation reaction by chlorine to chloroform formation. Even though hypochlorite addition is still thought to be the largest contributor of chloroform formation, chloroform production during both C- and E-stages should properly be evaluated since the both stages can produce lesser but comparable amounts of chloroform.

4.1. Introduction

A lot of volatile, low molecular weight chlorinated compounds, as well as high molecular weight chloro-organics, are produced during bleaching of pulp when chlorine-containing bleaching agents are used. Chloroform is produced at bleacheries as one of the major by-products to emit into the environment through atmosphere. Chloroform emission during hypochlorite bleaching stage (H-stage) is particularly serious so that in west European countries in the middle of 80's, H-stage process was totally eliminated from bleaching sequences. Chloroform formation during chlorination and alkali extraction stages (C- and E-stages) is also important to note. It is known that some reaction conditions during C-stage such as chlorine multiple, reaction temperature, reaction time, and the degree of chlorine dioxide substitution, are responsible for chloroform production.[1] It is also reported that chloroform precursors in C-stage effluent, when treated with alkali, can produce chloroform to a considerable degree so that chloroform production exponentially increases with the increase in pH of the effluent.[2] It is thought that this is due to chloroform precursors produced by chlorine treatment, which are easily hydrolyzed by alkali treatment to form chloroform. Possible chloroform formation can not, thus, be estimated accurately without treating chlorinated pulp and C-stage effluent under so strong alkali conditions as to hydrolyze all of the chloroform precursors. However, chloroform can easily be attacked by some nucleophiles such as OH^- under certain alkali conditions. It has been tested that some parts of chloroform can be converted rapidly to formic acid by a certain warm alkali.[3] Chloroform determination is, thus, rather hard and challenging, depending on the reaction conditions.

Appropriate methods to evaluate chloroform production during C- and E-stages are required, but another difficulty faces the researchers. Chloroform is so volatile compound with poor aqueous solubility that it is rather difficult to sample chloroform quantitatively without leakage. According to some investigations and evaluation presented by Japan Paper Association in 1997, chloroform emission to the atmosphere from pulp and paper industry in Japan arrives at around 1500 ton/year. But the chloroform production per pulp (by their evaluation basis) determined in their plant-scale investigations, shows low reproducibility (50-450 μg/g o.d. pulp) and they admit more precise determination methods are required.[4]

Headspace gas chromatographic analysis was applied as a simple technique to determine volatile organic compounds (VOCs), especially in the field of drinking water research[5-7]. Yet only a few attempts were made to apply headspace gas chromatography to the determination of volatile organic compounds in kraft mill streams[8] or in bleach effluents[9].

In this study, the elimination of chloroform leakage into the air during both reaction and sampling was tried. A gas-tight reaction vessel was used so that the accuracy and precision in the determination of chloroform would be improved. Quantitative evaluation of the maximum chloroform production during C- and E-stages was also investigated, based on the determination of chloroform potentially produced from its precursors generated in lignin during chlorination stage.

4.2. Experimental

4.2.1. Evaluation of the Possible Chloroform Formation from NUKP and NOKP during Both C- and E-stages

Well-washed unbleached softwood kraft pulp (NUKP) with a kappa number of 24 and oxygen-prebleached softwood kraft pulp (NOKP) with a kappa number of 11.3 were tested as samples (125mg each on o.d. weight basis). The sample was mixed with water and gently defibrated by a mixer. The sample together with a stirring magnet was put in a 100ml pressure-proof, gas-tight reaction vessel with a hollow screw cap to which inner lining coated with Teflon was attached (shown in Fig.4-1). The reaction vessel was sealed and put on a magnetic stirrer to stir the sample very well. A prescribed amount of chlorine water was added to the sample through inner lining with a microsyringe, so that chlorine multiple ranged from 0.10 to 0.20. Chlorine multiple is defined as the chlorine charge in percentage (% on pulp) divided by the kappa number of unbleached pulp. Chlorination was performed under room temperature (26-30°C) for 60min at 0.5% pulp consistency. The reaction was finished by adding 1.0ml of 0.2M $Na_2S_2O_3$ solution to the sample with a syringe, keeping the vessel sealed.

After the reaction, 2ml of saturated NaCl solution, a prescribed amount of 5g/l NaOH solution, and deionized water were sequentially added with a syringe to the sample in the sealed vessel, so that the total volume of the sample solution was set up to 30ml. NaOH dosage (% on pulp) was the sum of 2.5% on pulp (on o.d. weight basis) and twice the amount of the charged chlorine (on molar basis). Namely, NaOH charge of 5.20%, 6.56%, 7.91% on pulp was applied to the chlorinated NUKP samples

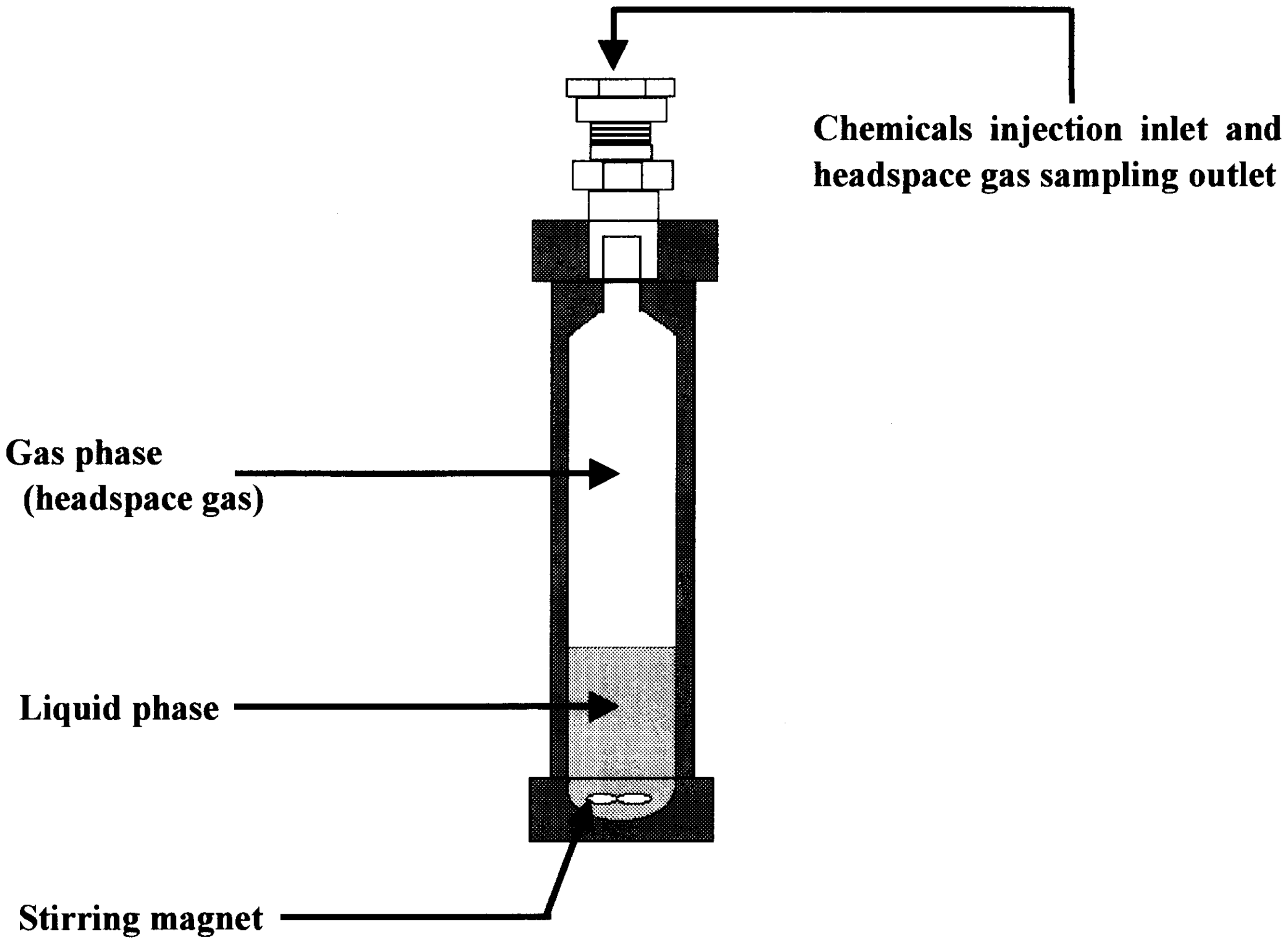


Fig. 4-1 A pressure-proof, gas-tight reaction vessel used in this experiment

with chlorine multiples of 0.10, 0.15, 0.20, respectively, whereas NaOH charge of 3.77%, 4.41%, 5.05% on pulp to the chlorinated NOKP samples with the corresponding chlorine multiples, respectively. After the NaOH addition, the reaction vessel was transferred to a water bath equipped with a stirrer. Warm alkali treatment was performed at 70°C for 60min.

After the alkali treatment, 1.0ml of headspace gas in the vessel was sampled with a gas-tight syringe. Headspace gas chromatographic determination of chloroform was performed using a gas chromatograph (GC-17A: SHIMADZU) equipped with a mass spectrometer (QP-5000: SHIMADZU) with single ion monitoring mode. The base ion peaks of chloroform (m/z = 83 and 85) were monitored. Temperature of the injection inlet and the detector were both set at 200°C. Helium was used as carrier gas. As a capillary column suitable for the separation of volatile organo-halogen compounds, AQUATIC (GL Science Inc., with the length of 60m and inner diameter 0.25mm, film thickness 0.4μm: coated with 75% dimethyl polysiloxane and 25% phenyl polysiloxane) was used. Temperature of column was kept at 40°C for 1min, programmed to 140°C at a rate of 5°C/min, then held for 2min at the temperature.

4.2.2. Separate Determination of Chloroform from Chlorinated Pulp and Chlorination Liquor

4.2.2.1. Chlorination of NUKP at 0.5% Pulp Consistency

NUKP (15g) was mixed with water and gently defibrated by a mixer. The sample together with a stirring magnet was put in a 5000ml Erlenmyer flask. The flask was put on a stirrer to stir the sample very well. A prescribed amount of chlorine water was added to the sample by a transfer pipet, so that chlorine multiple ranged from 0.10 to 0.20. The flask was then sealed with a Teflon stopper. Chlorination was performed under room temperature (26-30°C) for 60min at 0.5% pulp consistency. The reaction was finished by adding 120ml of 0.2M $Na_2S_2O_3$ solution to the sample. After 240ml of saturated NaCl solution was added, the sample was filtered to separate chlorinated pulp from chlorination liquor. Chlorination pulp was washed three times with 750ml each of deionized water. Chlorinated pulp and chlorination liquor were respectively stored at a cold room (4°C) until use.

Chlorinated pulp (125mg) was mixed with water and gently defibrated by a mixer. The sample was alkali-treated in the gas-tight reaction vessel to determine chloroform in the same manner as described above.

Chlorination liquor (25ml) was also treated with alkali in the vessel and chloroform in the headspace gas was determined by the above procedure.

Alkali charge for the pulp and the liquor was fixed at 10% on chlorinated pulp weight basis.

4.2.2.2. Chlorination of NUKP at 5% Pulp Consistency

4.2.2.2.1. Chlorination by pH-unadjusted Chlorine Water (Low pH)

NUKP (15g) was chlorinated with chlorine multiple ranging from 0.10 to 0.20 in a heavy duty, plastic bag so that chlorination conditions other than pulp consistency (5%) were the same as mentioned in section 2.2.1. After filtration, parts of chlorinated and water-washed pulp (125mg) and chlorination liquor (2.5ml) were separately treated by warm alkali in the reaction vessel. Alkali treatment and headspace gas analysis were performed by the procedure described above, but alkali charge for the pulp and the liquor each was fixed at 2.5% and 10% on chlorinated pulp basis (625 and 2500μl of 5g/l NaOH solution was use, respectively). Before subjecting to the warm alkali treatment, the chlorination liquor was diluted to 25ml of deionized water.

4.2.2.2.2. Chlorination by pH-adjusted Chlorine Water (High pH)

Chlorine gas was introduced into 250ml of 5g/l NaOH solution until the solution was saturated with chlorine to prepare a chlorine solution (pH 2.4: containing 11.6g/l of active chlorine as Cl_2). An aliquot of the chlorine solution (210ml) was diluted with 90ml of 5g/l NaOH solution to obtain a pH-adjusted chlorine water (adjusted to pH 5.7). NUKP (15g) was chlorinated by the pH-adjusted chlorine water in a heavy duty, plastic bag at pulp consistency of 5%. After filtration, parts of chlorinated pulp (125mg) and chlorination liquor (2.5ml) were separately treated by warm alkali in the reaction vessel. Alkali treatment and headspace gas analysis were performed by the procedure described as above, but alkali charge was fixed at 10% on chlorinated pulp.

Kappa numbers of NUKP, NOKP, chlorinated NUKPs, chlorinated and alkali-treated NUKPs, was measured according to TAPPI useful method (UM 246).

4.2.3. Chlorination and Alkali Treatment of Lignin Model Compounds

4.2.3.1 Treatment of MWL

Softwood (Japanese red pine; *P. densiflora*) MWL (4.5mg) prepared by the procedure of Björkman[10] was completely dissolved in 5.0g/l NaOH (10ml), thenadjusted pH below 7 (5.6-6.3) with 1.2mol/l HCl. The neutralized solution was then diluted by deionized water so that total volume of the liquid phase during chlorination reached to 25ml after a prescribed amount of chlorine water (depending on the chlorine multiples) was added to the sealed reaction vessel. Chlorination, alkali treatment, and chloroform determination in the headspace gas were performed in an above-mentioned manner.

4.2.3.2 Treatment of Guaiacol

Guaiacol (Wako Inc.: 2.8g) was dissolved in pure methanol to reach to the total volume of 20ml. A 20μl of the guaiacol-methanol solution was sampled with a microsyringe and injected in the sealed reaction. Chlorination (total volume of the liquid phase: 25ml), alkali treatment (30ml), and chloroform determination in the headspace gas were performed in an above-mentioned manner.

4.2.4. Preparation of Calibration Curve

Chloroform-methanol standard solutions containing 50-5000ppm of chloroform were prepared according to the "test method for volatile organic compounds in influents and effluents" provided by Japan Industrial Standard (JIS K 0125). These chloroform-methanol standard solutions (10-25μl) were separately used to prepare calibration curve after alkali treatment in the sealed reaction vessel. A prescribed amount of the standard solution, 26.3ml of deionized water, 1.0ml of 0.2M $Na_2S_2O_3$ solution, 2.0ml of saturated NaCl solution, and 625μl of 5g/l NaOH solution were added. The concentration of chloroform in the solution was set to correspond to the one when 20-700μg/g of chloroform is generated from 125mg of pulp. After the alkali treatment at 70°C for 60min, chloroform in the headspace gas was determined. Calibration curve was obtained from the relationship between peak area on the chromatogram and the concentration of chloroform, using least square method.

4.3. Results and Discussion

4.3.1. General Description

Shown in Fig.4-2 is the result that chloroform production after chlorination and alkali-treatment increases with chlorine multiple. In a different experiment where 2μl of liquid phase and/or 1ml of headspace gas were sampled at room temperature to determine chloroform in it immediately after chlorination, chloroform formation during chlorination stage without additional warm alkali treatment was estimated to be less than 10% of these values in Fig.4-2 (data not shown). These results proved that substantial amounts of the alkali-labile chloroform precursors were already generated in residual lignin in pulp after structural modification by chlorination, depending on chlorine multiple. Generally in an industrial standpoint, chlorination liquor is not subjected to warm alkali treatment under such a reaction condition as employed in this experiment. There are no previous studies dealing with warm alkali treatment of both chlorinated pulp and chlorination liquor, although they examined C-stage effluent adjusted to pH 7-12 by mixing it with black liquor, E-stage effluent or dilute NaOH solution at ambient temperature.[2] But nevertheless there is a possibility that chloroform precursors can be modified unexpectedly to form chloroform during some chemical and/or biological treatment processes of bleach effluent. Chloroform precursors in bleach effluent may be slowly hydrolyzed in the environment (i.e. in receiving water) even when not subjected to warm or strong alkali treatment. This is why the evaluation of chloroform precursors as a potential for chloroform formation matters. In this study chloroform precursors are estimated by warm alkali treatment, because it seems to be one of the simplest methods.

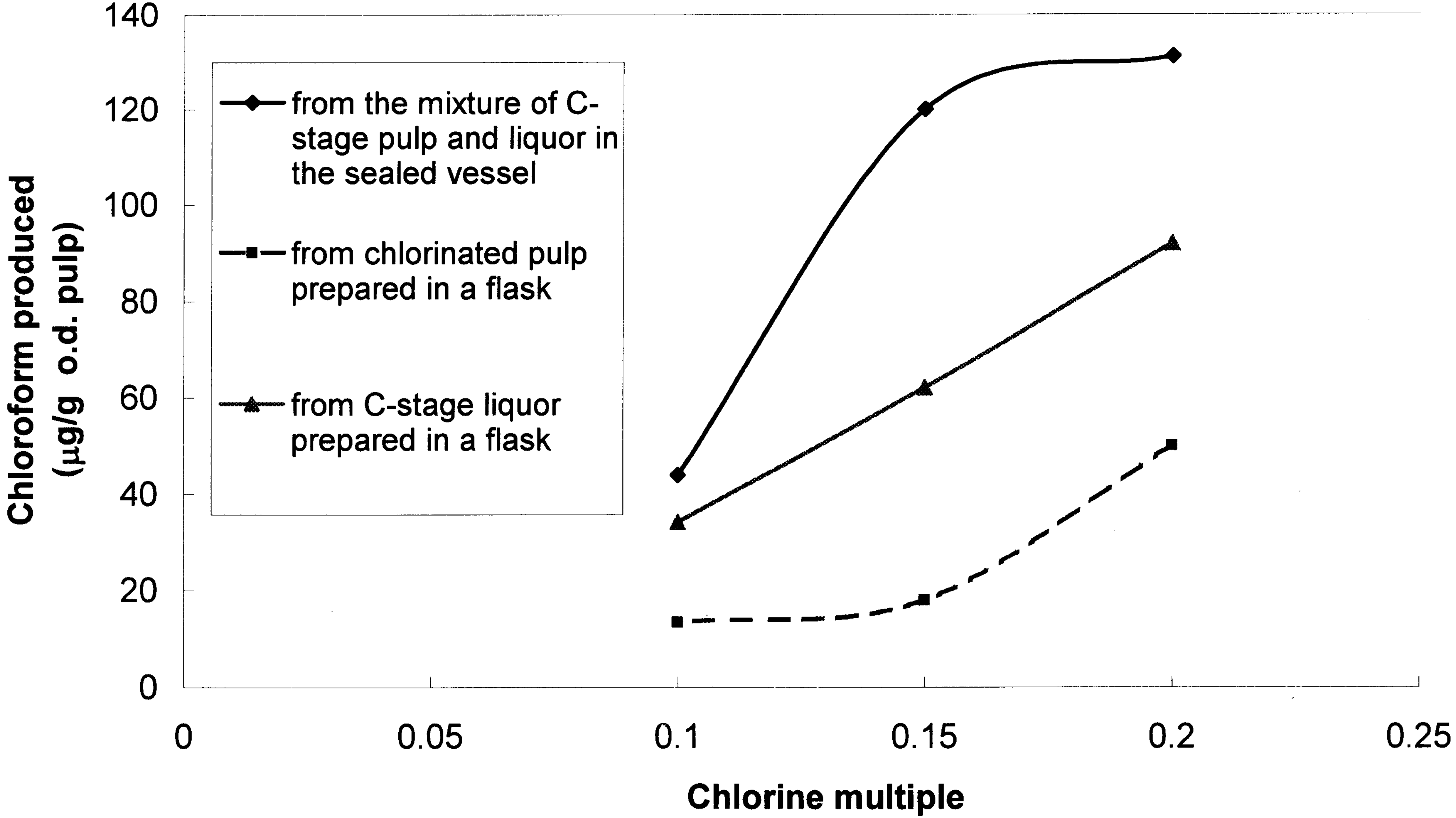


Fig. 4-2 Increase in chloroform formation with chlorine multiple when NUKP was chlorinated at the pulp consistency of 0.5% (after alkali treatment)

The sum of chloroform produced by warm alkali treatment of chlorinated pulp (125mg) and chlorination liquor (25ml), which were separately prepared from the chlorination of NUKP (15g) in an Erlenmyer flask at the pulp consistency of 0.5%, was not exactly the same but almost comparable to the amount of chloroform produced from NUKP (125mg) after successive chlorination (at the pulp consistency of 0.5%) and alkali treatment both in the sealed reaction vessel (Fig.4-2). In this experiment, the candidate had to use 125mg of chlorinated pulp and 25ml of chlorination liquor for the purpose of simplification of the procedure. Strictly, it can not be said that this was the same condition as when 125mg of NUKP was chlorinated and alkali-treated both in the reaction vessel. In addition, part of chloroform produced from chlorinated pulp and chlorination liquor may have been eliminated by filtration. In spite of the experimental difference between the two cases, it was found almost the same magnitude of chloroform formation after alkali treatment was expected.

The sum of chloroform produced by warm alkali treatment of chlorinated pulp and chlorination liquor, which were separately prepared from the chlorination of NUKP in a heavy-duty, plastic bag at the pulp consistency of 5%, was a little bit lower than the amount of chloroform produced from NUKP after successive chlorination (at the pulp consistency of 0.5%) and alkali treatment both in the sealed reaction vessel (Fig.4-3). This may be partly due to the elimination of part of chloroform produced during chlorination by filtration. The progress of chloroform formation may be changed between the two cases, depending on the reaction condition of chlorination. Almost the same magnitude of chloroform formation after alkali treatment, however, was expected in the two cases.

The result of chloroform formation plotted against the reduction in kappa number for chlorinated NUKPs (Fig.4-4) would be suggestive. Little or no formation of

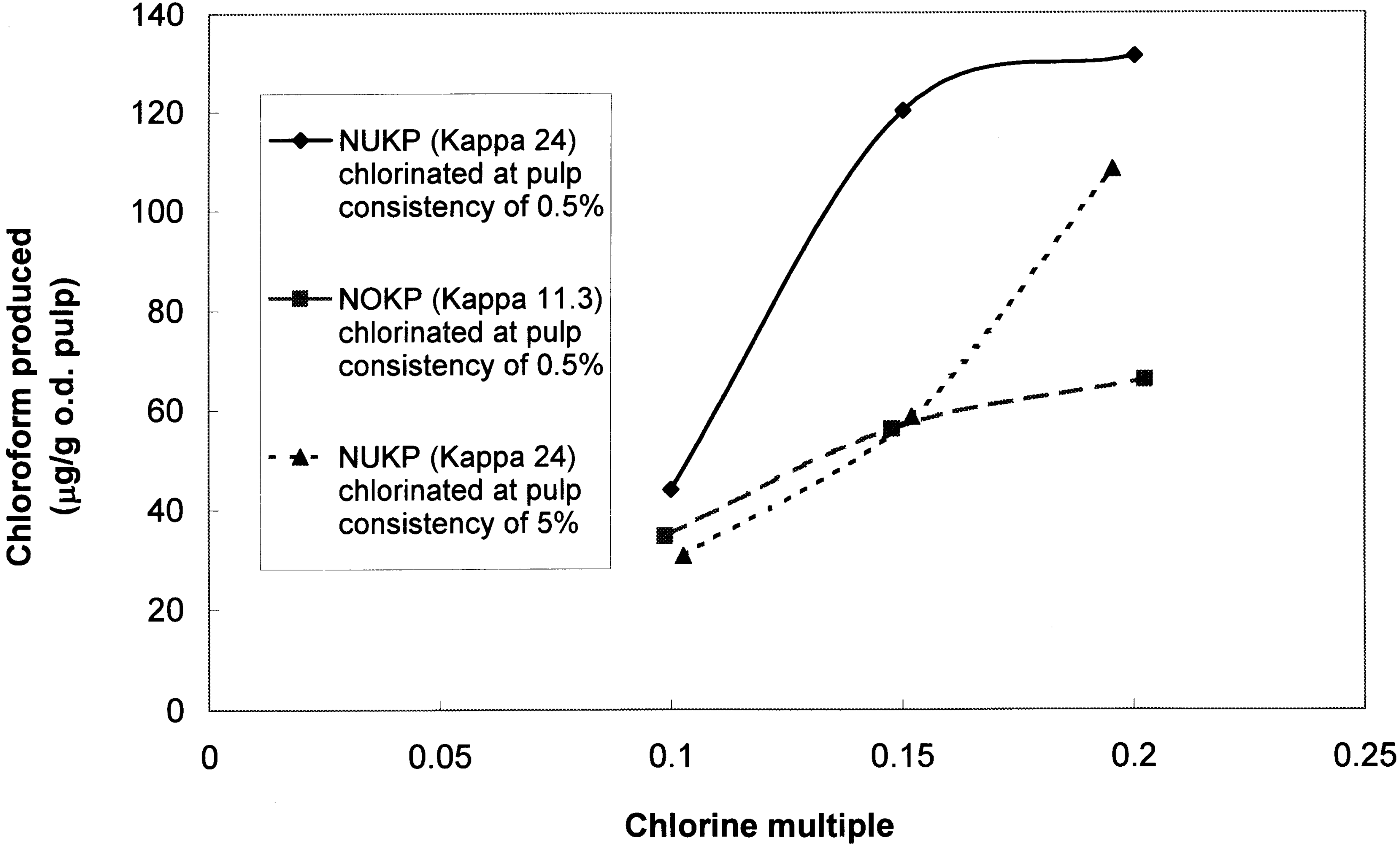


Fig. 4-3 Chloroform formation by the bleaching of NUKP and NOKP

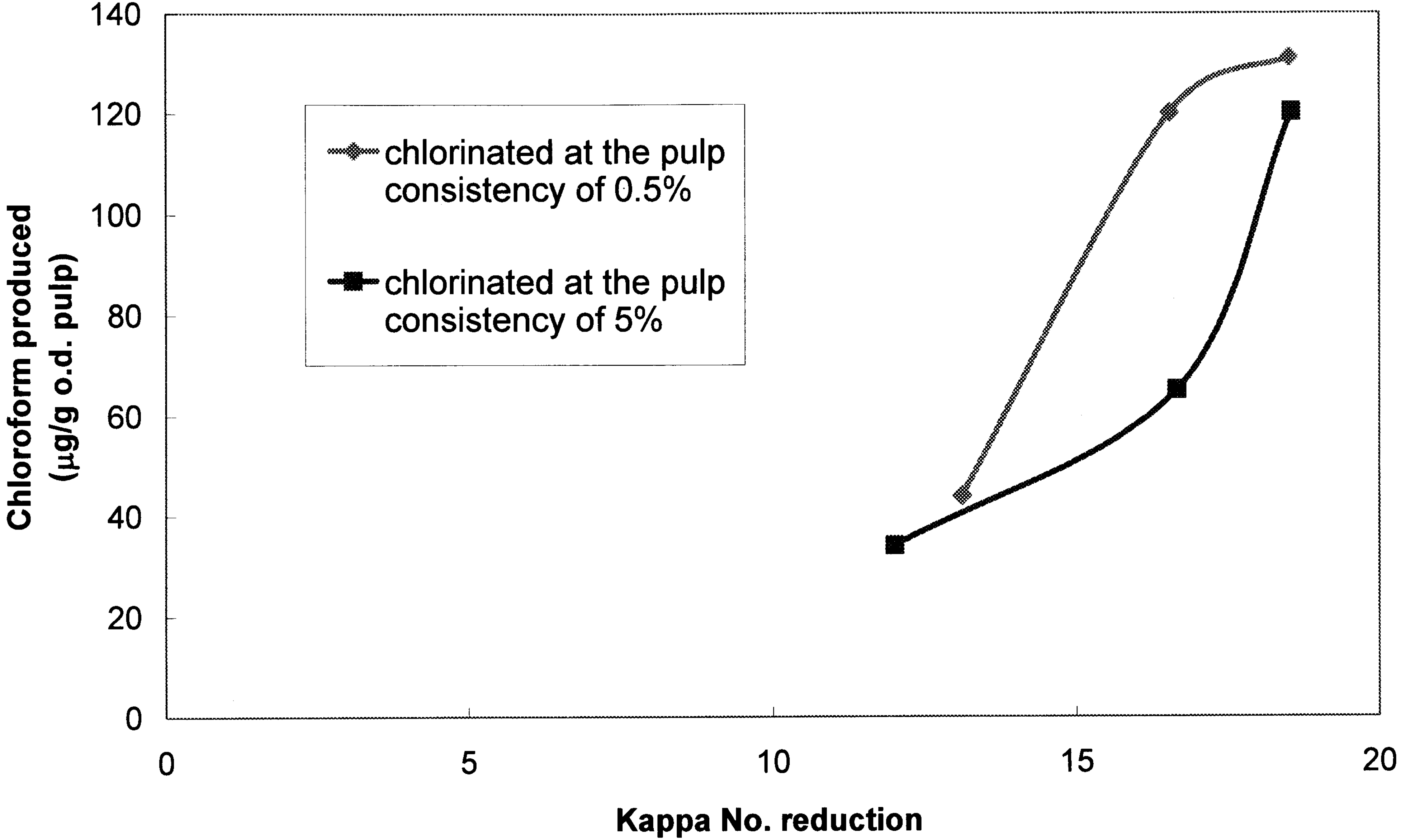


Fig. 4-4 Chloroform formation vs kappa number reduction

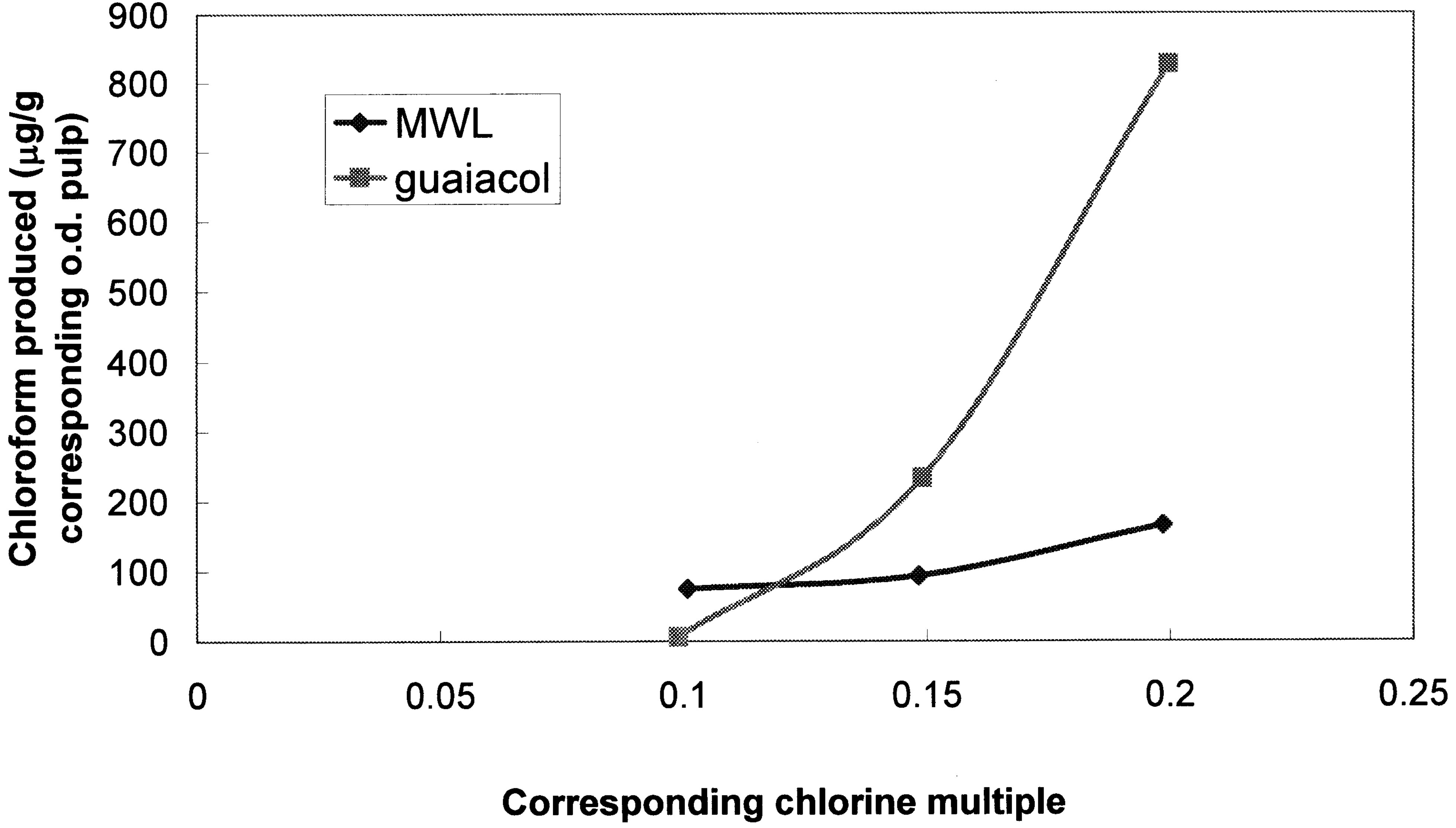


Fig. 4-5 Chloroform formation from softwood MWL and guaiacol by chlorination and alkali treatment

chloroform and its precursors can be expected if a mild reaction condition of chlorination, under which the reduction in kappa number of less than 10 is achieved during C- and E-stages, is employed. It seems clear that chloroform formation requires a certain degree of chlorination and oxidation reaction.

The results shown in Fig.4-3 also illustrate that with chlorine multiple ranging from 0.10 to 0.20, chloroform formation per kappa number of pulp ranged from 2 to 6μg/g o.d. pulp, or 1 to 4μg/mg lignin in pulp, regardless of oxygen prebleaching. Crawford *et al* reported from their plant-scale investigation that there appears no significant difference in chloroform generation between facilities (bleach lines) with and without oxygen delignification process.[11] Their result suggests that chloroform generation from kraft pulps with and without oxygen prebleaching depends largely on chlorine factor, but not on kappa number (lignin content) of pulp before chlorination, which seems contradictory to the result of the candidate's laboratory-scale experiment. The result by the candidate, using well-washed pulps (NUKP and NOKP) and chlorine water containing no chlorine dioxide, shows that chloroform production depends on kappa number as well as chlorine multiple (Fig.4-3). This discrepancy can be attributed to the difference in reaction and sampling conditions. The reaction temperature of chlorination, the degree of ClO_2 substitution in C-stage, pulp washing efficiency (or the degree of carryover of oxidized substances to C-stage that are produced during oxygen prebleaching stage), and the degree of chloroform leakage into the air are assumed to be different between the two results. These factors seem to affect greatly chloroform production during C- and E-stages, which was confirmed by the recent investigation by Iimori *et al.*[12]

Softwood MWL (4.5mg) was chlorinated and treated with alkali in the same manner as the low consistency (0.5%) treatment of pulp, using the reaction vessel (Fig.4-5).

MWL was used so that the weight of it corresponds to that of residual lignin in 125mg of the NUKP used in this study. Figs.4-3 and 4-5 show that whether MWL or residual lignin in pulp is used as a lignin sample, almost the same order of magnitude of chloroform formation can be expected from a prescribed amount of lignin, though the result of MWL gave slightly higher chloroform formation. The result also illustrates that lignin is exclusively the source of chloroform formation.

However, chloroform formation from the treatment of guaiacol as a lignin monomer model compound shows a different plot curve from that of MWL. This result was quite strange because almost the same molar ratio of guaiacol (2.8mg = 22.6μmol) to MWL (4.5mg = 22.5μmol) was intentionally sampled when equivalent molecular weight of 200 is applied for MWL. Virtually no chloroform or its precursors were produced when small amount of chlorine was charged to guaiacol even after alkali treatment. For example, when 42.4μmol of chlorine was applied to 22.6μmol of guaiacol, which corresponds to the chlorine charge multiple of 0.10 for NUKP with a kappa number of 24, chloroform formation was approximately 6μg/g of corresponding o.d. pulp, indicating the formation of chloroform and/or its precursors accounted for only 0.028mol% of guaiacol. Guaiacol has no side chain, which is structurally different from MWL. Thus it can serve more sites to which chlorine can attach by aromatic substitution reaction. At a low chlorine charge, chlorine was too rapidly consumed by the substitution reaction to produce chloroform and/or its precursors. At a high chlorine charge (chlorine multiple 0.20), on the contrary, enormous amount of chloroform was produced. This is because aromatic substitution reaction was first occurred exclusively, then followed by demethoxylation and oxidation to form phenolic hydroxyl, carbonyl, and carboxyl groups that are required to form chloroform precursors. Phenolic hydroxyl group of guaiacol is feasible to oxidation by chlorine to form carbonyl (quinone) and carboxyl structures. It is probable that this leads to afford enormous amount of chloroform precursors easily, if sufficient amount of chlorine is available for oxidation reaction.

An attempt was made to clarify the effect of oxidation reaction by chlorine on chloroform formation. As known from early studies,[13,14] chlorination of pulp at high pH amplifies oxidation reaction and suppresses substitution reaction. In chapter 2, stress was put on the important role of oxidation reaction by chlorine in delignification and lignin degradation. Again in this study, the candidate used pH-adjusted chlorine water (pH 5.7: described as "High pH" in Fig.4-6) by which chlorination under oxidation-favorable condition was achieved. Addition of NaOH to chlorine water shifts the following equilibrium (1) to the right to form hypochlorous acid (HClO), which is more effective to oxidation reaction than elemental chlorine (Cl_2) *per se*.

$$\mathbf{Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HClO} \qquad \ldots(1)$$

Under the reaction condition employed, HClO is exclusively the predominant reactant among active chlorine species.[13,14] Chloroform formation under high pH condition of chlorination (Fig.4-6) suggests that oxidation reaction by chlorine seems to enhance chloroform formation. This is partly explained by the formation of carbonyl (quinone) and carboxyl structures by HClO to form chloroform precursors, followed by alkali hydrolysis. But hypochlorite (ClO^-) treatment seems to produce much more chloroform than Cl_2 or even HClO treatment followed by warm alkali treatment, by the comparison with previous studies.[1,2,11,12,15] Chloroform formation per kappa number, or lignin content of kraft pulp by ClO^- treatment is much higher than those by Cl_2 and HClO treatment. But it should be noted that before chlorinated and alkali-extracted

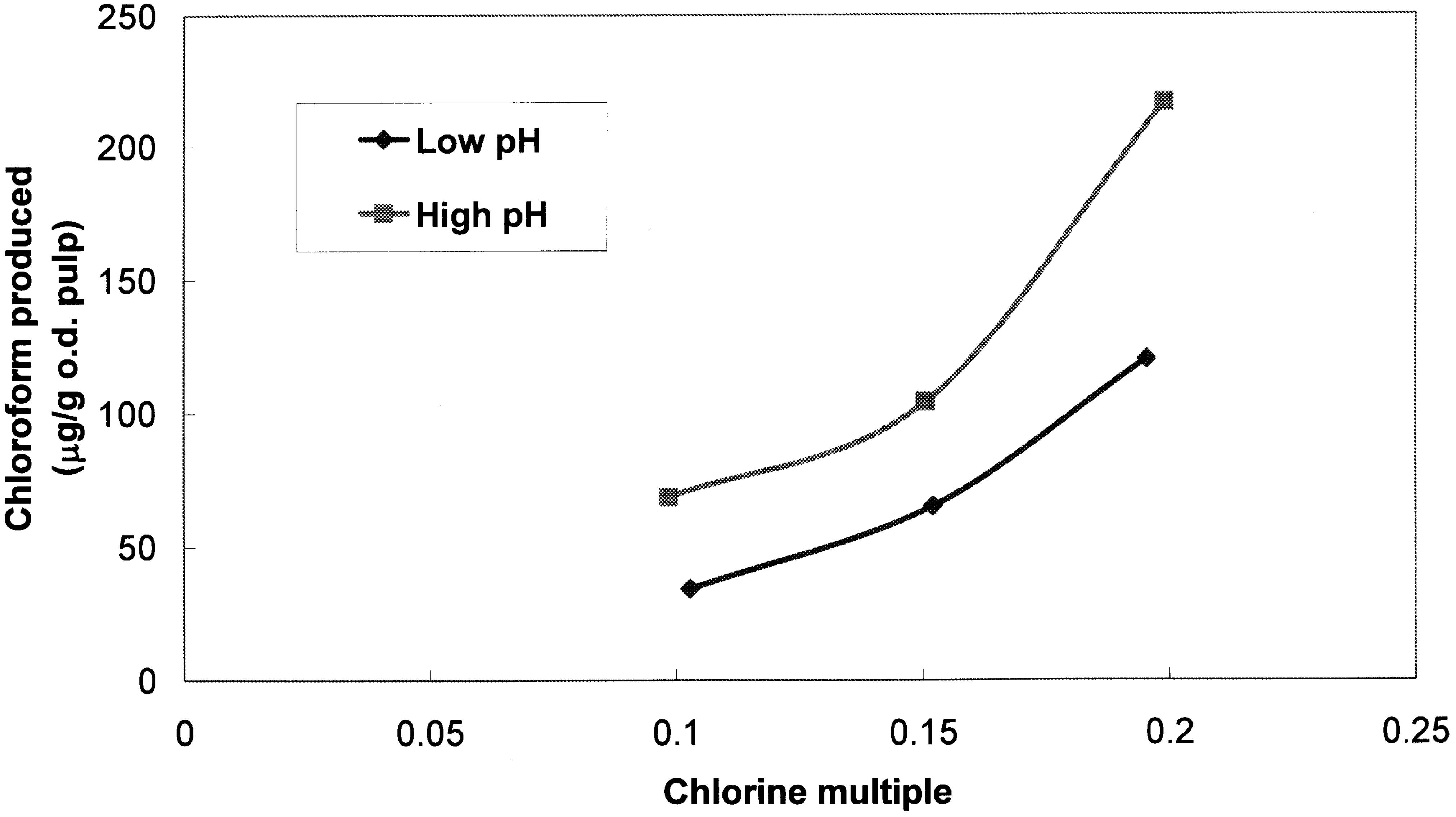


Fig. 4-6 Chloroform formation when NUKP was chlorinated by pH-adjusted and pH-adjusted chlorine waters

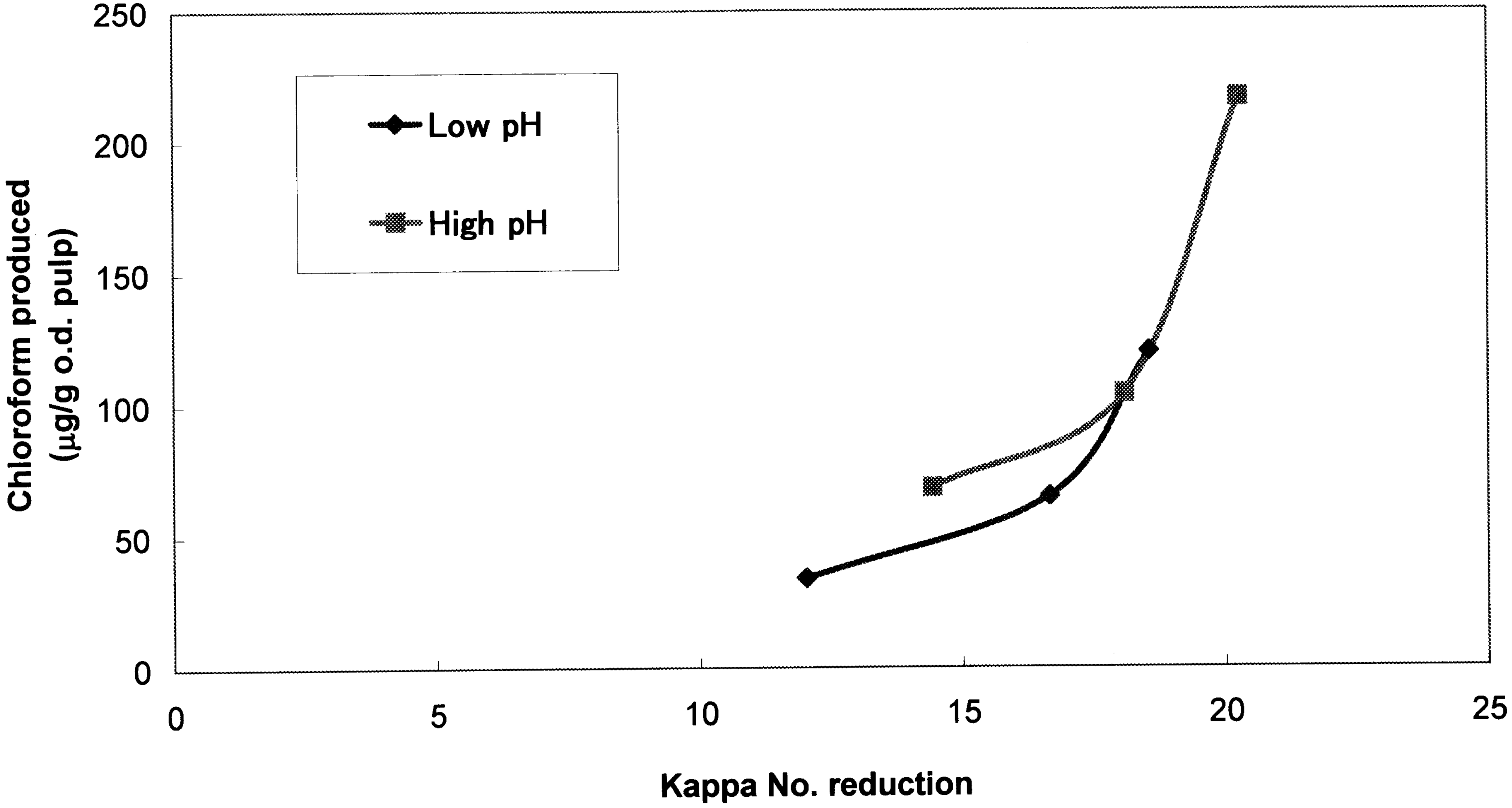


Fig. 4-7 Chloroform formation in relation to kappa number reduction when NUKP was chlorinated by pH-adjusted and pH-unadjusted chlorine waters

kraft pulp is subjected to H-stage, residual lignin content of the pulp is much lower than that of unbleached pulp. Therefore, even though hypochlorite bleaching stage (H-stage) is still thought to be the largest contributor of chloroform formation, both C- and E-stages can give comparable, if not greater, amounts of chloroform. This has been verified quite recently by Iimori *et al.*[12]

In Fig.4-7, chloroform formation under both chlorination conditions was plotted against the kappa number reduction after chlorination and warm alkali treatment. Similar curve plots were obtained for both reaction conditions. There is a certain threshold for the formation of chloroform and its precursors during C-stage to increase exponentially. It is suggested that chlorine is consumed ineffectively for delignification beyond the threshold during C-stage, only to produce enormous amount of chloroform precursors. Therefore, it is clear that extensive reduction in kappa number under severe chlorination condition can lead to drastic, undesired increase in chloroform formation. Chlorine multiple should be reduced for chlorine bleaching in order to minimize chloroform formation.

4.3.2. Comment for the Analytical Procedure and the Reliance of This Experiment

The procedure of headspace gas chromatographic analysis used in this study is basically according to the standard procedure, JIS K 0125. But parts of it were performed with some modification, since it would be simpler for the alkali treatment. According to JIS K 0125, it is recommended that headspace gas chromatography/mass spectrometry should be performed with a reaction vessel (i.e. a screw vial) heated at 60°C for 30min to force almost all the VOCs in liquid phase to gas phase (headspace). In this experiment, the reaction temperature of alkali treatment was higher (70°C) than those provided by the standard and the prolonged reaction time (1hr) was employed. The standard (JIS K 0125) also recommends that gas phase should account for 15-60% of the total volume (gas and liquid phase) in the vessel, while the gas phase during sampling in this experiment accounted for 70%. All of these differences, however, do not seem to give any serious problems to the accuracy of the determination in this study. This is partly because the reaction temperature used in our study (70°C) was well beyond the boiling temperature of chloroform (61-62°C). It is also known that gas chromatographic response of chloroform, which directly affects the accuracy of its determination, is relatively less affected by the proportion between gas and liquid phase than that of other halocarbon compounds[6,7].

Moreover, it is recommended according to JIS K 0125 that excessive amount of NaCl should be added to the liquid sample (i.e. 3g NaCl should be added to 10ml of sample solution) before heating so that chloroform in NaCl-saturated liquid phase can be effectively forced to gas phase by salting-out effect. This procedure can improve the yields of chloroform detected and minimize the detection variables which seem to

Table 4-1 Final pH after alkali treatment of the samples

	Sample Identification	Chlorine Multiple	Final pH
A	mixture of C-stage pulp and liquor (prepared in the sealed vessel), chlorination of NUKP: pulp consistency of 0.5%, using pH-unadjusted chlorine water, alkali treatment: charged NaOH varies with chlorine multiple	0.10	**11.1**
		0.15	**11.0**
		0.20	**11.0**
B	C-stage pulp (prepared in an Erlenmyer flask), chlorination of NUKP: pulp consistency of 0.5%, using pH-unadujusted chlorine water, alkali treatment: charged NaOH varies with chlorine multiple	0.10	**11.1**
		0.15	**11.0**
		0.20	**11.0**
C	C-stage liquor (prepared in an Erlenmyer flask), chlorination of NUKP: pulp consistency of 0.5%, using pH-unadujusted chlorine water, alkali treatment: charged NaOH varies with chlorine multiple	0.10	**11.0**
		0.15	**11.0**
		0.20	**11.0**
D	mixture of C-stage pulp and liquor (prepared in the sealed vessel), chlorination of NOKP: pulp consistency of 0.5%, using pH-unadjusted chlorine water, alkali treatment: charged NaOH varies with chlorine multiple	0.10	**11.0**
		0.15	**11.0**
		0.20	**10.9**
E-1	C-stage pulp (prepared in a plastic bag), using pH-unadjusted chlorine water (Low pH) at pulp consistency of 5%, alkali treatment: 2.5% NaOH charge	0.10	**10.6**
		0.15	**10.6**
		0.20	**10.5**
E-2	C-stage liquor (prepared in a plastic bag), using pH-unadujusted chlorine water (Low pH) at pulp consistency of 5%, alkali treatment: 2.5% NaOH charge	0.10	**10.5**
		0.15	**9.0**
		0.20	**4.6**
F-1	C-stage pulp (prepared in a plastic bag), using pH-unadjusted chlorine water (Low pH) at pulp consistency of 5%, alkali treatment: 10% NaOH charge	0.10	**11.6**
		0.15	**11.5**
		0.20	**11.5**
F-2	C-stage liquor (prepared in a plastic bag), using pH-unadujusted chlorine water (Low pH) at pulp consistency of 5%, alkali treatment: 10% NaOH charge	0.10	**11.6**
		0.15	**11.6**
		0.20	**11.5**
G-1	C-stage pulp (prepared in a plastic bag), using pH-adjusted chlorine water (High pH) at pulp consistency of 5%, alkali treatment: 10% NaOH charge	0.10	**11.7**
		0.15	**11.7**
		0.20	**11.8**
G-2	C-stage liquor (prepared in a plastic bag), using pH-adujusted chlorine water (High pH) at pulp consistency of 5%, alkali treatment: 10% NaOH charge	0.10	**11.8**
		0.15	**11.7**
		0.20	**11.6**
H	MWL (chlorinated and alkali-treated in the sealed vessel), 10% NaOH charge on corresponding pulp weight basis	corresp. multiple 0.10	**11.4**
		corresp. multiple 0.15	**11.1**
		corresp. multiple 0.20	**10.7**
I	guaiacol (chlorinated and alkali-treated in the sealed vessel), 10% NaOH charge on corresponding pulp weight basis	corresp. multiple 0.10	**11.6**
		corresp. multiple 0.15	**11.4**
		corresp. multiple 0.20	**11.3**

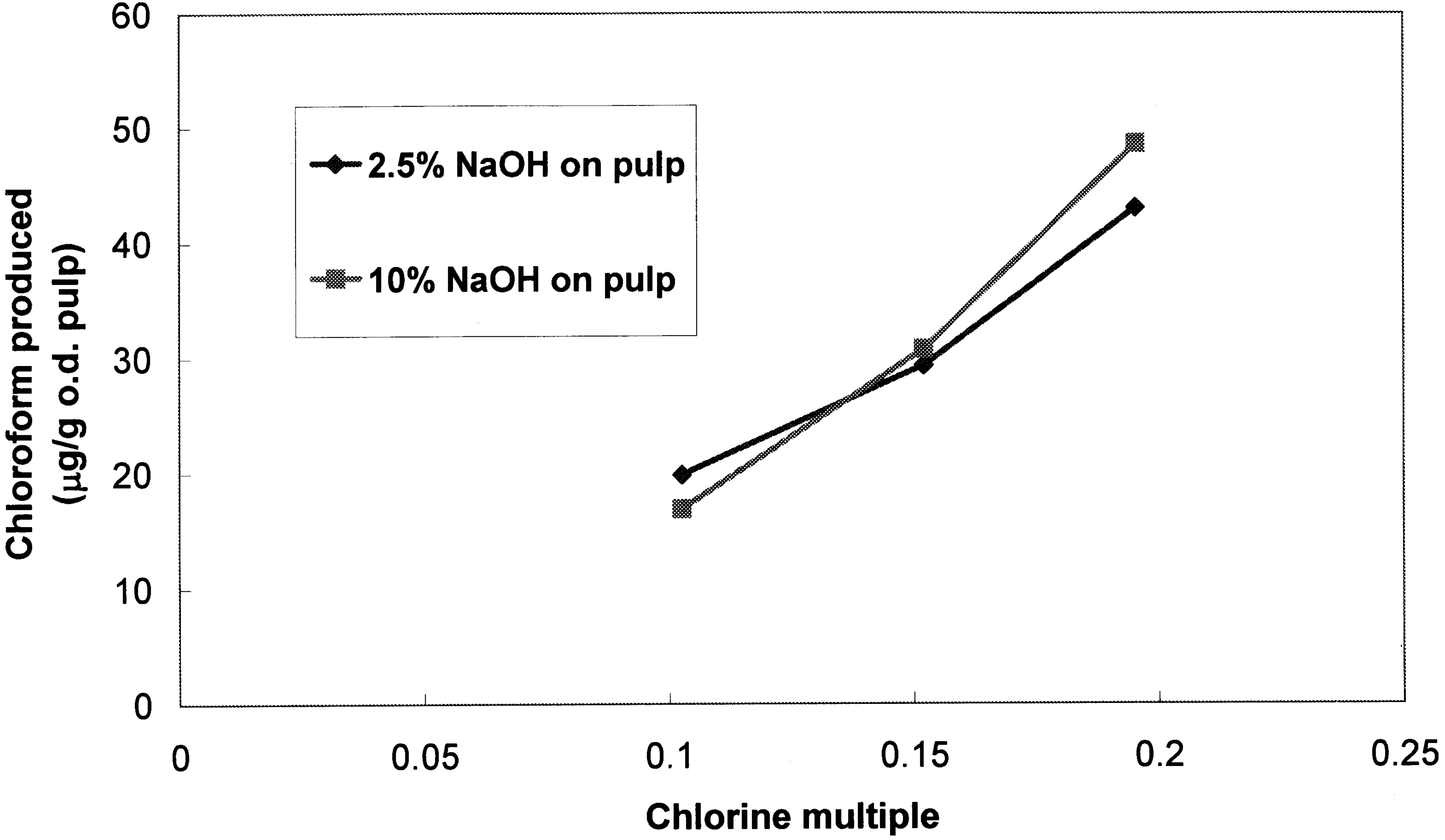


Fig. 4-8 Chloroform formation when chlorinated NUKP was treated by different charge of NaOH

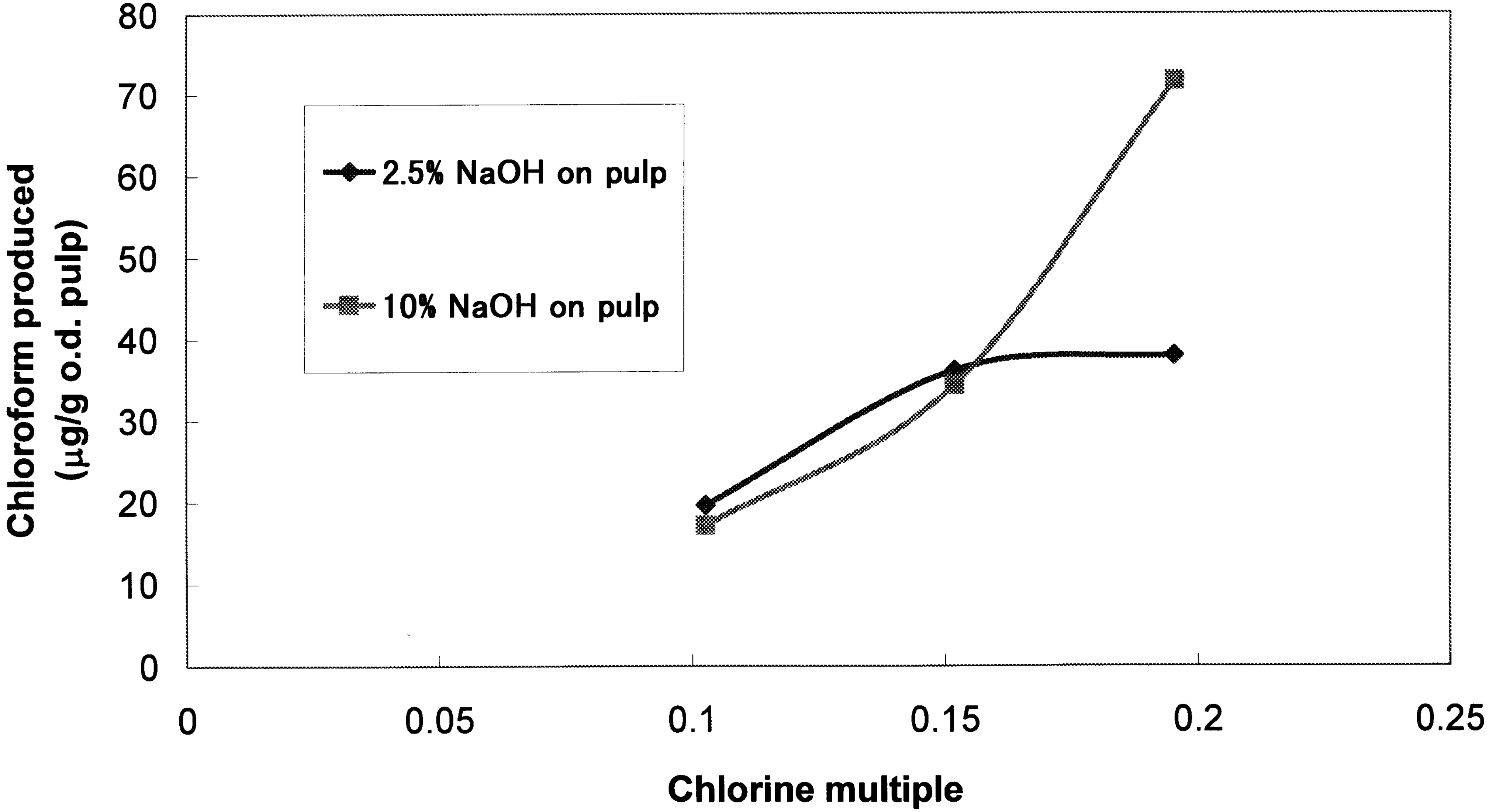


Fig. 4-9 Chloroform formation when chlorination liquor was treated by different charge of NaOH

Table 4-2 Change in chloroform formation with prolonged reaction time of warm alkali treatment

	Sample Identification	Chlorine Multiple	Reaction Time (min)	GC Peak Area	Chloroform Produced (μg/g pulp)
A	mixture of C-stage pulp and liquor, prepared in the sealed vessel, chlorination of NUKP: pulp consistency of 0.5%, using pH-unadjusted chlorine water, alkali treatment: charged NaOH varies with chlorine multiple	0.10	60	478843	42.4
			105	539514	48.4
			150	573810	51.9
		0.15	60	1219785	116.5
			105	1259111	120.4
			150	1395139	134.0
		0.20	60	1381282	132.6
			105	1403459	134.8
			150	1421587	136.6
B	C-stage pulp, prepared in an Erlenmyer flask, chlorination of NUKP: pulp consistency of 0.5%, using pH-unadujusted chlorine water, alkali treatment: charged NaOH varies with chlorine multiple	0.10	60	194276	13.9
			105	256716	20.1
			150	not determined	-
		0.15	60	252805	19.8
			105	288631	23.3
			150	not determined	-
		0.20	60	529981	47.5
			105	653494	59.8
			150	not determined	-
C	C-stage liquor, prepared in an Erlenmyer flask, chlorination of NUKP: pulp consistency of 0.5%, using pH-unadujusted chlorine water, alkali treatment: charged NaOH varies with chlorine multiple	0.10	60	399690	34.4
			105	427999	37.3
			150	471123	41.6
		0.15	60	693604	63.8
			105	720556	66.5
			150	723266	66.8
		0.20	60	1037406	98.2
			105	979102	92.4
			150	1016169	96.1

depend on the different concentrations of salt contained in the different samples. It is not, however, appropriate for the purpose of this study to add excessive amount of NaCl to the sample before chlorination, because even slight amount of chloride (Cl^-) can shift the equilibrium (1) (shown in the previous section 4.3.1.) to the left to cause to change the reaction condition of chlorination. Therefore in this experiment, no sodium chloride was added to the samples before chlorination. Even before alkali treatment in this experiment, it is also impossible to add that much of NaCl without opening the sealed reaction vessel, or without any leakage of chloroform. But the candidate thought that the concentration of NaCl in the liquid phase should be kept as constant as possible to all the samples. Saturated NaCl solution was, therefore, added to all the samples with a syringe through inner lining before alkali treatment, keeping the vessel sealed. The saturated NaCl solution (2ml) containing 0.63g of NaCl was used, which corresponded over 50 times the amount of NaCl produced when the samples were subjected to alkali treatment. It can, thus, be said that detection variables caused by NaCl concentration of the samples were successfully minimized in this study, although salt concentration is one of the key factors when headspace gas chromatography is performed[7].

In this experiment, final pH of the samples after warm alkali treatment at 70°C ranged from 10.5-11.8 with a few exceptions (Table 4-1). The candidate tried to see the effect of NaOH charge to the accuracy and precision of chloroform determination. The result in Fig.4-8 shows that chlorinated pulp (prepared at 5% pulp consistency during chlorination), if washed very well before alkali treatment, gives almost the same amount of chloroform when treated by warm alkali. Such difference of alkali charge (2.5% and 10% on pulp) seems to have no effect on the quantitative estimation of chloroform precursors in chlorinated pulp under reaction condition employed in this study. But as shown in Fig.4-9, this is not true to chlorination liquor. In the previous study[11], it was reported that virtually all the chloroform intermediates or precursors were converted to chloroform at pH 10.5. In the case of chlorination liquor samples prepared by the chlorination of NUKP at 5% pulp consistency with chlorine multiples 0.15 and 0.20, the final pHs were lower after the warm alkali treatment with 2.5% alkali charge on chlorinated pulp basis (Table 4-1). It is clear that insufficient alkali charge leads to the underestimation of chloroform formation. From those experiments, it is again supported that appropriate estimation of possible chloroform formation requires a certain threshold degree of alkali charge. This is the reason the candidate usually employed 10% NaOH charge on pulp for the quantitative estimation of possible chloroform formation. But in the candidate's earlier experiments in this chapter, NaOH charge was changed, depending on the chlorine multiple for different samples, to achieve a constant final pH (adjusted to pH 11). The experiment using a fixed NaOH charge on samples is, needless to say, much easier to perform than that using a changed NaOH charge, and thus should be employed if almost the same degree of chloroform formation is expected in both cases.

Some of the samples showed a moderately increased and/or decreased chloroform formation when prolonged reaction time of warm alkali treatment was employed (Table 4-2). Under these conditions, chloroform formation from its precursors and structural conversion of chloroform are thought to occur competitively. Reaction time employed in this experiment (1hr) may be a little too short to hydrolyze all the chloroform precursors to give maximum chloroform formation. In addition, part of chloroform in alkali solution is modified to such a compound as formic acid, which needs further investigation.[3] These may more or less affect the precision of each determination. But the influence of these competitive reactions in this study at a fixed reaction time (1hr) on the chloroform determination was proved to be minor because these results by the candidate had relatively a good reproducibility (5-15%), compared to the reproducibility reported in JIS K 0125 (10-20%).

In our preliminary experiments, it was usually observed less than 5% of chloroform still remained in the liquid phase (data not shown). Another experiment, using chloroform-methanol standard solution and a modified α-cellulose prepared by successive warm sulfuric acid treatment and cold alkali treatment of full-bleached softwood kraft pulp, showed that chloroform adsorption to pulp had practically no effect on the precision of the experiment (data not shown). Chlorine treatment of chloroform-methanol standard solution in a different experiment illustrated that structural conversion of chloroform by chlorine treatment under acidic condition is negligible (data not shown). Therefore, it is safely stated that chloroform determination after chlorine and alkali treatment under the reaction condition employed in this study is fairly successful and reliable.

4.4. Conclusions

Headspace gas chromatography/mass spectrometry was successfully applied to the determination of chloroform. The formation of chloroform and/or its precursors during C- and E-stages was quantitatively estimated, using a pressure-proof, gas-tight reaction vessel, without any gas leakage. By this laboratory-scale study, it is accurately shown that a definite amount of lignin can produce a definite amount of chloroform and its precursors if treated by a definite amount charge of chlorine (1 to 4 μg/mg lignin in pulp). No significant effect of oxygen prebleaching on the reduction in the formation of chloroform precursors per kappa number was observed. Oxygen-prebleaching can contribute chloroform formation only in a sense that it can reduce absolute lignin content of kraft pulp before chlorine bleaching, leading to the reduction in the formation of chloroform precursors. The evaluation in this study showed basically a good coincidence with the plant-scale study recently reported by Iimori et al,[16] although they used oxygen-prebleached softwood kraft pulp to determine chloroform in bleach effluent by solvent extraction gas chromatography. It was clarified in this study that there was a certain threshold of chlorination condition, beyond which exponentially increased chloroform formation was observed. It was suggested that the progress of oxidation reaction by chlorine is a key to the formation of chloroform and its precursors. It was thought that mild reaction condition of chlorination was required for the purpose of reduction, even if not elimination, of chloroform emission to the atmosphere. It was concluded that the sum of chloroform formation during C- and E-stages can never be negligible, but almost comparable to that during H-stage. C- and E-stage effluents containing chloroform and/or its precursors should properly be treated before emitted to the environment.

5. Origin of Alkane-Type Structure Detected by the Analytical Pyrolysis of Oxidized Lignins

Summary: Analytical pyrolysis (pyrolysis-gas chromatography/mass spectrometry: Py-GC/MS) was applied to the analysis of oxidized lignins to seek specific peaks of their own origin. Oxidized lignins supplied a specific peak pattern on gas chromatogram (pyrogram), which proved to be a series of homologous compounds carrying alkane-type structure. It is indicated that alkane-type structure derives from a certain kind of extractives of unbleached softwood kraft pulp (NUKP), not from partial structure of oxidized lignin. Contrary to the drastic modification of lignin aromatics under oxidative reaction conditions, the compounds with alkane-type structure showed relatively high resistance toward oxidation. Although the peaks that derive directly from a specific structure of oxidized lignins were not detected, the GC peak ratio, AL/AR, meaning the ratio of some representative compounds with alkane-type structure (AL: wood extractives origin) to those with aromatic structure (AR: lignin origin), was found to be a good indication of the degree of oxidation that oxidized lignins underwent.

5.1. Introduction

Numerous amounts of modified lignin have been discharged to the environment from pulp bleaching mills. It is very important and urgent to establish the whole knowledge of high molecular weight chloro-organics discharged to the environment, although chlorine-bleaching technology adopted worldwide has already been starting to lose its status. High molecular weight chloro-organics show only a little biodegradability so that they might stay in the environment persistently to produce lower molecular weight chloro-organics with more toxicity gradually for a long period of time. The study on these substances is of greater importance especially in Japan because chlorine-bleaching process is still employed as a major bleaching sequence. Even if the current bleaching technology based on the chlorine delignification is converted to non-chlorine bleaching technology, the discharge of the modified lignin will continue unless a totally closed mill system is established. Therefore, it is still an important task to establish an analytical method for discharged lignin. Most of the lignin analytical methods usually employed in the field of wood chemistry, such as nitrobenzene oxidation, acidolysis, thioacidolysis, or methylation-potassium permanganate oxidation, are based on the aromatic structure of lignin. Modified lignins such as found in the bleaching effluent are hardly analyzed by these conventional methods because they are extensively oxidized and their aromatic nature is already lost. Pyrolysis gas chromatography (Py-GC) applied so far to lignin analysis is also based on the aromatic nature of lignin.[1-13] However, if oxidized lignin can give specific peaks on pyrogram due to oxidatively cleaved aromatic rings, pyrolysis GC is expected to provide a simple and rapid technique as an analytical tool for high molecular weight oxidized lignins discharged to the environment.

In the present study, some oxidized lignins were examined by pyrolysis GC combined with mass spectrometry and a finding of characteristic pyrolysis products that were observed commonly in all oxidized lignin samples (chlorine-, oxygen-, ozone-oxidized lignins) is discussed. Some application of analytical pyrolysis as a promising tool for estimating the degree of oxidative modification of lignin-derived samples, is discussed.

5.2. Experimental

5.2.1. Materials

Some lignins and oxidized lignins, as models for the residual lignin of the bleached kraft pulp, were prepared to be tested.

Chlorolignin was extracted from chlorine-bleached softwood kraft pulp (chlorine multiple was 0.15) by extraction of chlorinated and water-washed pulp (CW-NKP) with dioxane-water mixture (45:55) at room temperature for 24hrs.[14] The ratio of CW-NKP to aqueous dioxane was 1g to 20ml. The extraction was repeated three times and the extract was concentrated by evaporation under vacuum at 42°C, and recovered by lyophilization.

Oxygen-oxidized lignin was prepared by the oxygen-alkali treatment of isolated kraft pulp residual lignin (IRL: preparation procedure is shown below). IRL (1.5g) was dissolved in 300ml of an aqueous alkali solution containing 6.0g sodium hydroxide and 6ml of nitric acid solution containing 1000ppm Fe^{3+}. The solution was heated to 95°C and held for a desired time at the temperature under 1.0MPa of oxygen pressure. Periodically (60, 180, and 3000min), 20ml of the solution was taken from the reaction vessel. The solution was neutralized to pH 5 by hydrochloric acid and dialyzed against deionized water at room temperature, by the use of cellulose tube (Viskase Sales Corp.; cut off molecular weight 3500). The dialysate was concentrated under vacuum at 42°C and recovered by lyophilization. In a separate experiment, the solution prepared by the same procedure was subjected to the measurement of permanganate consumption, according to the procedure by Tong *et al.*[15]

Ozone-oxidized lignin was prepared by the ozone-treatment of IRL (preparation procedure is shown below). IRL (22mg) was dissolved in a dilute alkali solution and neutralized to pH 7.3 by dilute hydrochloric acid. The final volume was 20ml. Oxygen gas containing 3% of ozone (checked by iodometric titration) was bubbled into the solution in an ice bath (0-3°C) at a flow rate of 20ml/sec for 15min, the use of an ozone generator (ON-3-2; Nippon Ozone Co., Ltd.). The ozonated sample was dialyzed against deionized water at room temperature, by the use of the cellulose tube mentioned as above (cut off level was 3500). The dialysate was concentrated under vacuum at 42°C and recovered by lyophilization.

Extraction of the kraft pulp residual lignin (IRL) was performed by the use of aqueous dioxane containing hydrochloric acid (0.2mol/l HCl : dioxane = 1 : 4) under reflux temperature.[16]

As reference samples of "less modified" lignin, milled wood lignin (MWL) was used. The MWL was prepared by the extraction of finely ground softwood wood meal (Japanese red pine; *P. densiflora*) and purified according to the procedure of Björkman[17]).

A part of MWL (170mg) was dissolved in aqueous acetic acid (glacial acetic acid : deionized water = 10ml : 0.5ml). In an ice bath, chlorine-acetic acid solution (2ml) was added to the MWL solution. The chlorine-acetic acid solution was prepared by introducing chlorine gas into glacial acetic acid (containing 62.3g/l of Cl_2). The chlorination of MWL was performed at 18°C for 60min. At the end of the reaction, nitrogen gas was bubbled into the solution for 15min in an ultrasonic cleaner (BRANSONIC model 5210 J; Emerson-Japan Inc.) to reduce residual Cl_2. The chlorinated sample was concentrated under vacuum at 42°C, then recovered by lyophilization.

Another part of MWL (10mg) was dissolved in a mixture of glacial acetic acid, deionized water and methanol (16ml : 3ml : 1ml). The MWL solution was ozonated for 5min by the procedure mentioned above (see the ozsonation of IRL). The ozonated sample was concentrated under vacuum at 42°C, then recovered by lyophilization.

Extractives of kraft pulp were also served as samples. Well-washed unbleached softwood kraft pulp (20g on oven-dry weight basis) was extracted in 200ml of distilled acetone. The extraction was performed in a sealed grass bottle with a Teflon screw cap at 60°C for 3hrs, and repeated three times. The acetone soluble extract was concentrated to syrup (50mg) within the temperature range of 30-35°C. Part of the oily syrup (10mg) was dissolved in a mixture of acetic acid and water ($AcOH:H_2O$ = 9:1) and treated by ozone for 1min and 5min. Other reaction conditions of ozonation are the same as in the case of ozone-oxidized lignin (above-mentioned).

5.2.2. Analytical Condition

Microfurnace pyrolyzer (PYR-4A: SHIMADZU) connected with gas chromatograph (GC-17A: SHIMADZU) and mass spectrometer (QP-5000: SHIMADZU) was used. NEUTRA-BOND 1 (GL Science 30m×φ0.25mm, film thickness: 0.4 μm) was used as a non-polar capillary column. Column temperature was kept at 50°C for 1 minute, then raised to 270°C at a rate of 5°C/min. Pyrolysis was performed at 500°C. The amount of each sample injected at one operation was 30-300 μg.

5.3. Results and Discussion

5.3.1. Peak Pattern Characteristics of Pyrograms from Oxidized Lignin Preparations

The most significant structural feature commonly observed among pyrolysis products of all the oxidized lignins was alkane-type structure, which was checked by the mass fragmentation pattern of each pyrolysis product (discussed later). As shown in Fig 5-1, the majority of pyrolysis products obtained from chlorolignin were found to carry alkane-type structure as their structural skeleton. A similar tendency is clearly seen on the pyrograms of oxygen-oxidized and ozone-oxidized lignins (Fig.5-2). Those alkane-type structures can never be seen on the pyrogram of softwood MWL, suggesting those structure does not exist originally in lignin (Fig.5-1). Instead, a lot of peaks from aromatic structure of lignin are found on the pyrogram of MWL, as observed in various lignin preparations.[18] Some peaks carrying alkane-type structures, as well as many aromatic peaks, were detected in the pyrogram of isolated residual lignin of softwood kraft pulp (IRL), but only in a limited number.

As an example, the mass fragmentation pattern of a peak, which appears at the retention time of 24.9min on the pyrogram, is shown on the top in Fig.5-3. The mass fragmentation signals starting from 55 atomic mass unit (m/z 55) with 14 intervals were clearly observed. This is the characteristic fragmentation pattern of alkane structures.[19] The same fragmentation pattern is observed in many peaks of the pyrograms of oxidized lignin samples. Those peaks on a pyrogram appear at regular intervals of retention time, indicating that they are a series of homologous alkane-type compounds. In ^{1}H-NMR spectra of these oxidized lignin samples, the signals corresponding to those

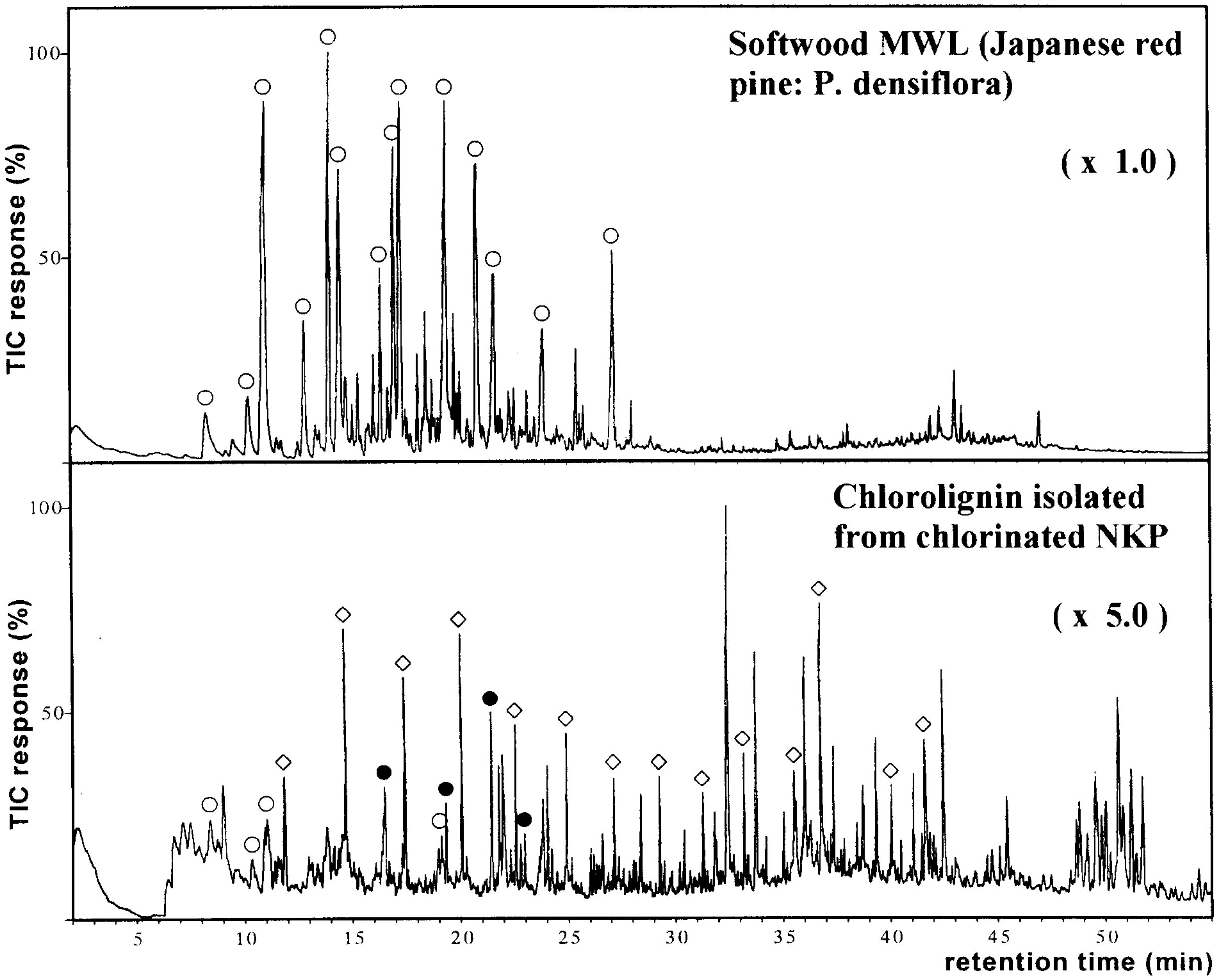


Fig. 5-1 Total ion chromatograms of MWL and chlorolignin

○:pyrolysis products carrying aromatic structure

●:pyrolysis products carrying chlorinated aromatic structure

◇:pyrolysis products carrying alkane-type structure

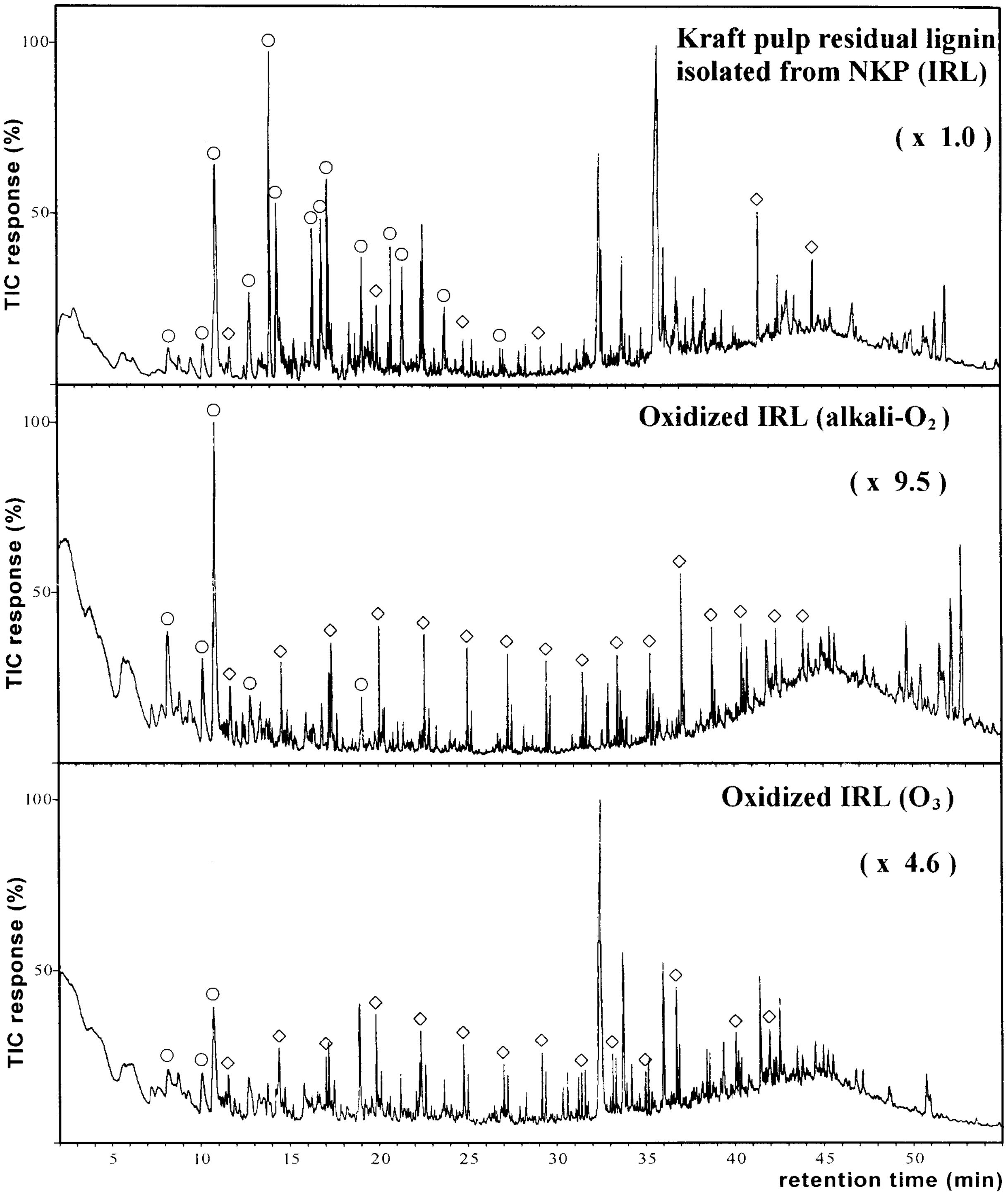


Fig. 5-2 Total ion chromatograms of isolated kraft pulp residual lignin (IRL), oxidized IRL by alkali-oxygen oxidation, and oxidized IRL by ozonation

○:pyrolysis products carrying aromatic structure

◇:pyrolysis products carrying alkane-type structure

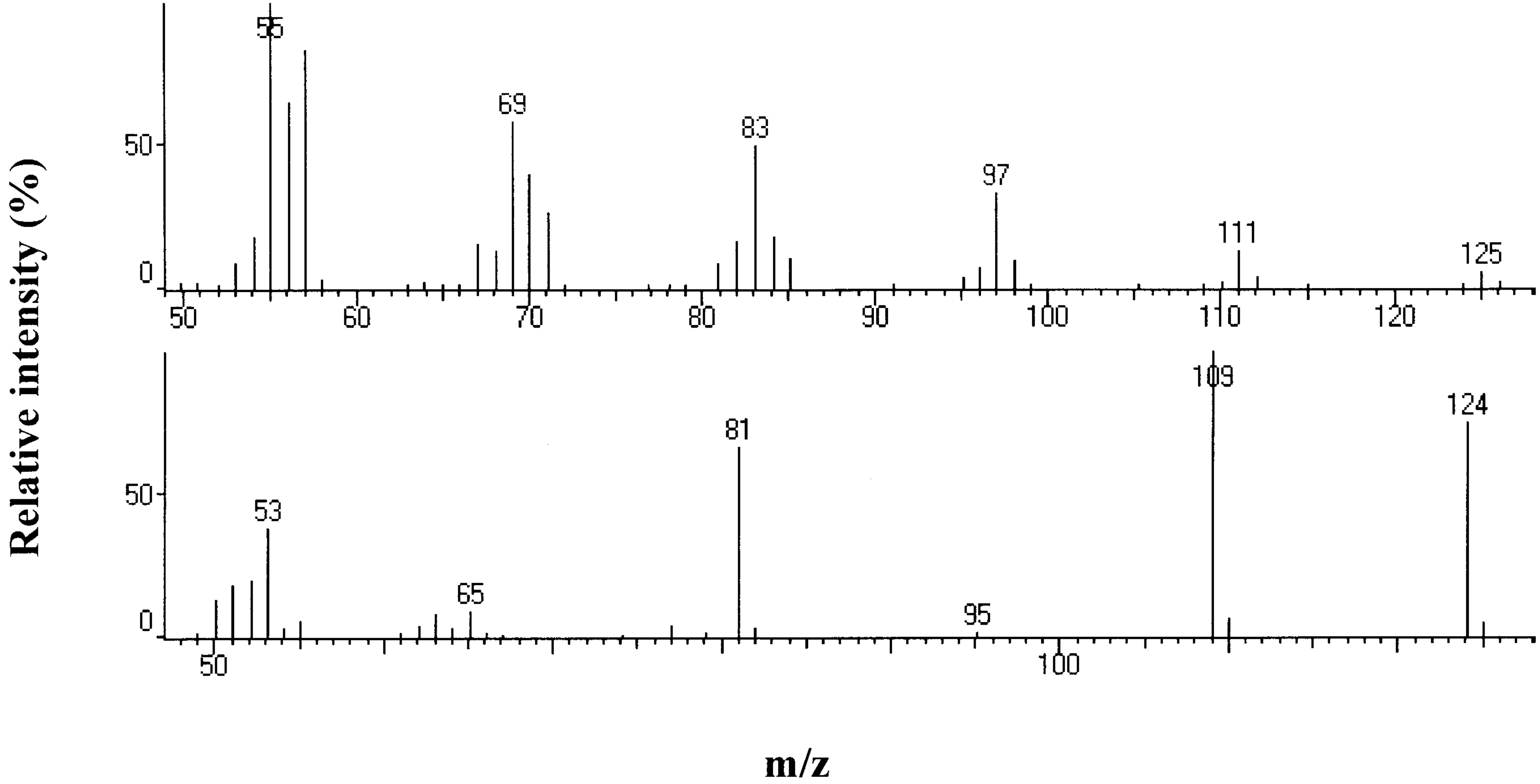


Fig. 5-3 Mass spectra of alkane-type compounds (top) and guaiacol (bottom)

alkane structures were observed only as minor peaks (data not shown), indicating that these alkane-type structures are not originally present in oxidized lignins as a main structural feature.[20] Those alkanes was thus thought to be produced *in situ* by hydrogenative reaction from some common precursors during pyrolysis. As such precursors, a muconic acid type structure or similar type structures produced by oxidative ring opening reaction of aromatic nuclei were most presumably hypothesized (Fig.5-4: top). However, a simple model experiment by the use of *trans, trans*-muconic acid did not give such alkane-type structures on pyrogram (Fig.5-4: bottom). Chlorinated catechol did not give such an alkane-type structures, either. Chlorinated or ozone-treated MWL gave little or no alkane-type structure on their pyrograms (data not shown). Speculation for the origin of such alkane-type structure had to be greatly modified (Fig.5-4). The alkane-type structure may be introduced from other components of pulp such as extractives, rather than directly from oxidized structure of lignin, which will be discussed later.

However, the similarity in pyrolysis products between chlorolignin and other oxidized lignins indicates that these modified lignins have a common structural feature. It was suggested from this result that the progress of oxidative reactions not only during oxygen or ozone bleaching but also during chlorine bleaching can be observed by Py-GC/MS.

In 1991, Loon and co-workers[21] reported a result of analytical pyrolysis on the water of the river Rhine into which pulping mill effluent was discharged. In a figure of pyrolysis-mass (Py-MS) spectra of high molecular weight materials isolated from some pulp mill effluents shown in the paper, the presence of alkane-type structures was already implied. However, there was no description about this. Thus, alkane-type

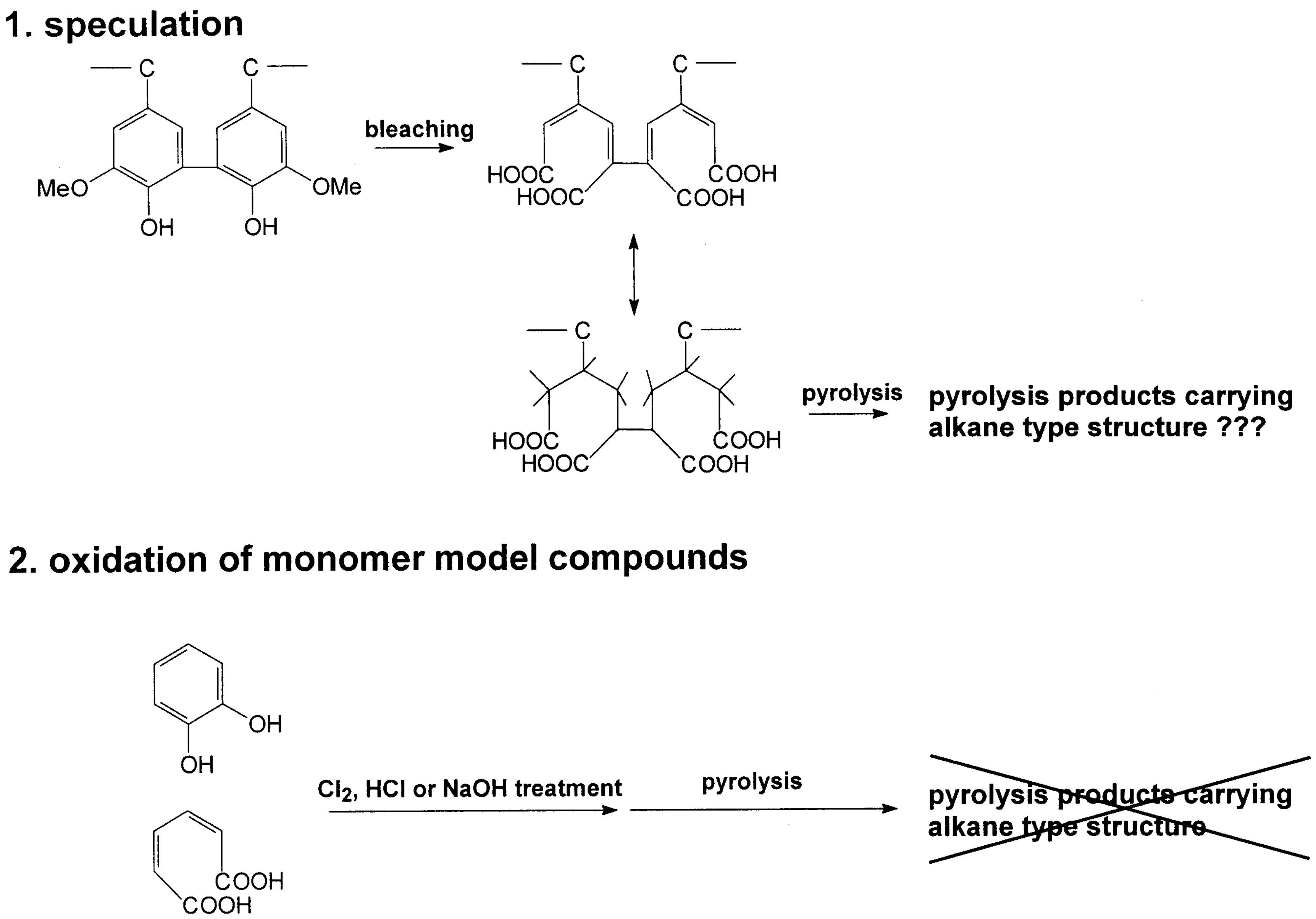


Fig. 5-4 Speculation for the formation of precursors carrying alkane-type structure from oxidized lignin

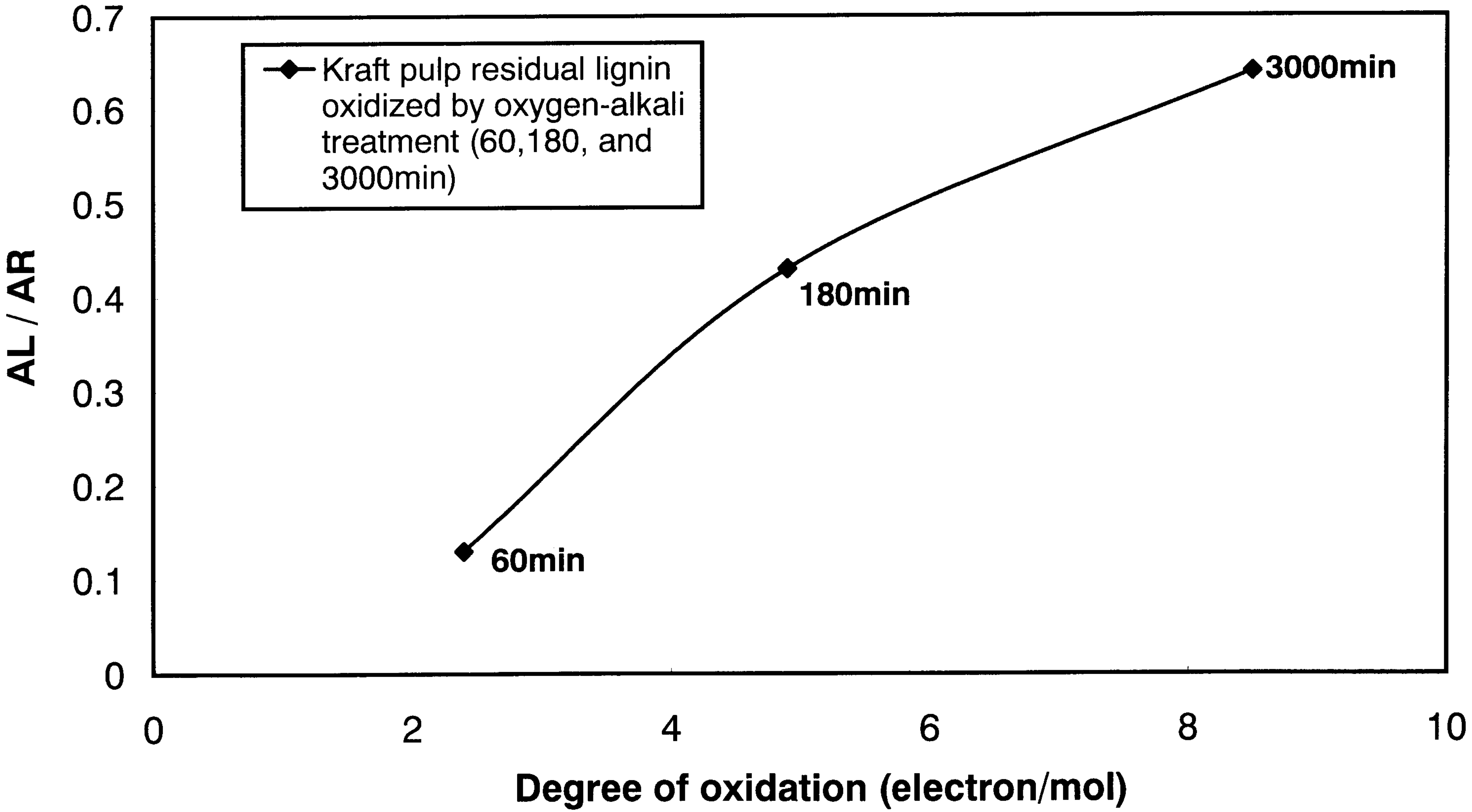


Fig. 5-5 Relationship between the progress of oxidation and peak area ratio of alkane-type compounds to aromatics (AL/AR) on GC

structures were not considered to be a significant feature of pyrolysis products of oxidized lignins.

But if there is a certain relationship between the relative peak intensity of alkane-type structures and the degree of oxidation oxidized lignins underwent, analytical pyrolysis can be a promising tool for the analysis of modified lignin preparations. The relationship is shown in Fig.5-5. Degree of oxidation that oxygen-oxidized lignins underwent was estimated by the difference of permanganate consumption between IRL and oxygen-oxidized IRLs. The permanganate consumption is converted to the number of electrons that can be abstracted from lignin structural unit. As an indication of the relative peak intensity of alkane-type structures, the value (AL/AR) is estimated. AL represents the total peak area of the top eight peaks carrying alkane-type structure, while AR stands for the sum of peak area of the top ten peaks carrying aromatic structure of lignin. Significant relationship between the degree of oxidation the oxidized lignin underwent and the peak area ratio of AL to AR (AL/AR) were observed, indicating the value AL/AR is a good indicator for the structural modification of lignin preparations under some oxidizing condition of bleaching. It is concluded that analytical pyrolysis can be applied to observe the degree of oxidative modification of lignin.

5.3.2. Pyrograms of Extractives of Pulp

The pyrogram of acetone-soluble extract from NUKP is shown at the top of Fig.5-6. A specific peak pattern of alkane-type structure can be observed . If this specific peak pattern derives from certain extractives of unbleached kraft pulp, it is probable that this specific pattern was produced as a result of the survival of some of such extractives when kraft pulp residual lignin was almost completely decomposed under oxidizing reaction condition of bleaching. It was requested to investigate whether these extractives are more stable by the attack of some oxidizing bleaching agents than lignin aromatics. In Fig.5-6, pyrograms of ozone-oxidized acetone-extract from pulp are illustrated. The peak with relatively strong intensity at the retention time of 40min, clearly seen on the pyrogram of acetone-extract before ozone treatment, can no longer be observed on the pyrograms below. It is assumed that this is a component that is labile to ozone-oxidation. However, the specific peak pattern can, on the whole, be clearly observed for all the pyrograms shown in Fig.5-6. Strictly speaking, the intensity of the series of specific peaks seems reduced gradually with the progress of oxidation reaction by ozone if absolute intensity is properly estimated by the division of relative peak intensity by charged sample weight. In a preliminary experiment, ozone-oxidized MWL gave no peak of lignin aromatics. Together with these results, it is suggested that the acetone-soluble extractives of pulp are more stable than lignin aromatics when subjected to ozone treatment under the same reaction condition. Some parts of wood extractives seem to survive bleaching condition, and thus relative intensity of the peaks derived from them seems gradually increasing with the progress of oxidative modification of aromatics. This is also due to the fact that relative intensity, not absolute intensity, of peaks is displayed on pyrogram. As for the fate of

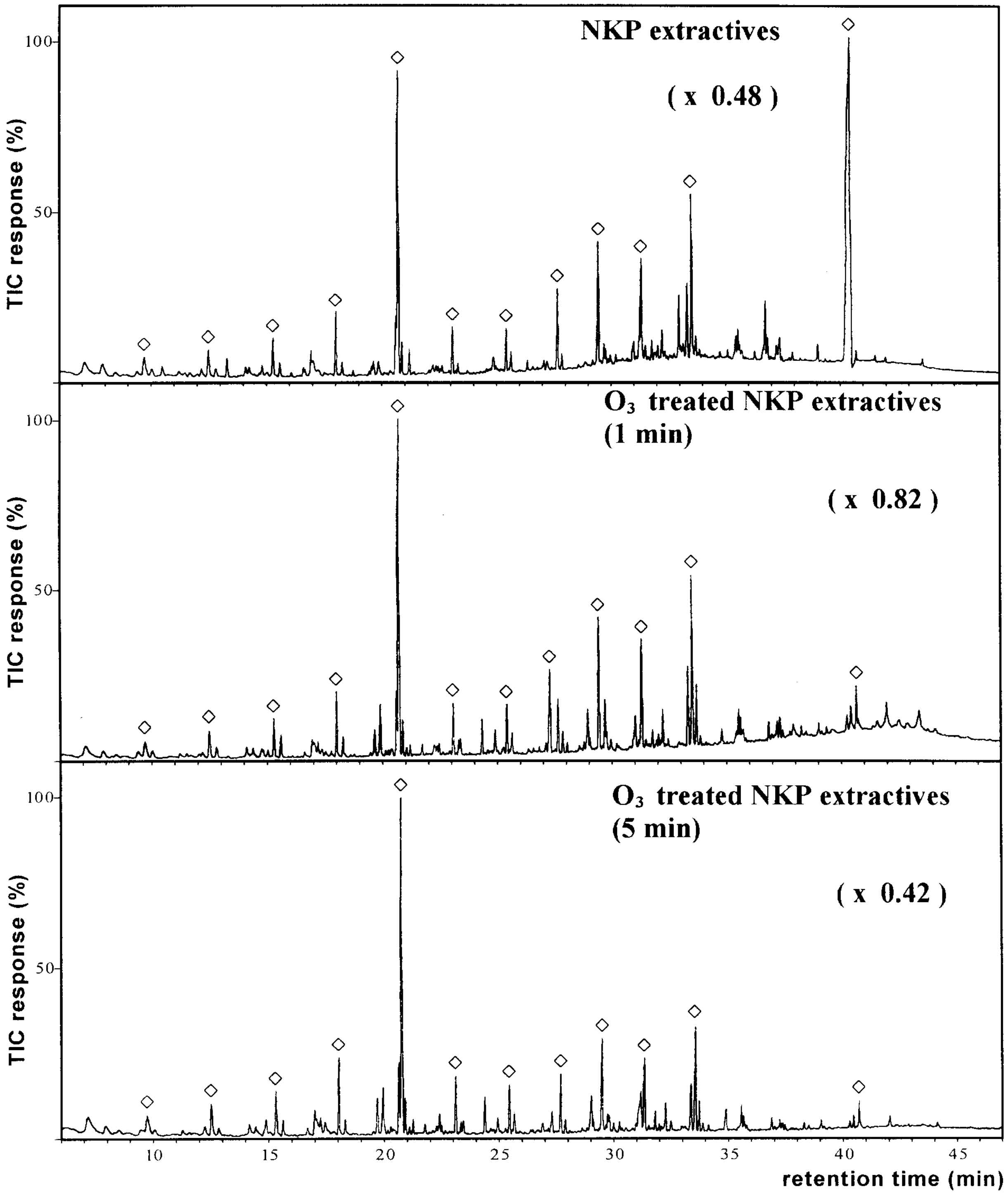


Fig. 5-6 Total ion chromatograms of the pulp extractives and oxidized extractives by ozonation

◇:pyrolysis products carrying alkane-type structure the extractives of pulp subjected to the bleaching sequences, some researchers have proposed several reports quite recently[22,23].

It is supported strongly from this experiment that the specific peak pattern on pyrogram is derived from certain extractives, not from a specific structure of oxidized lignin.

5.4. Conclusions

Chlorolignin isolated from chlorinated soft wood kraft pulp and other oxidized lignin preparations, as well as extractives of unbleached pulp whose origin is assumed to be wood extractives, were analyzed to investigate if analytical pyrolysis can also be applied to the analysis of high molecular weight components of chlorine bleaching effluent. A lot of low molecular weight aromatics (AR) were detected from a lignin preparation such as MWL by this method, while only small amount of them was detected from oxidized lignins. It was, however, observed that oxidized lignins gave a specific peak pattern of their own on pyrogram. This was ascribed to a series of compounds carrying alkane-type structure (AL). Significant relationship between the degree of oxidation the oxidized lignin underwent and the peak area ratio of AL to AR (AL/AR) were observed, indicating the value AL/AR is a good indicator for the structural modification of lignin preparations under some oxidizing condition of bleaching. It was concluded that analytical pyrolysis can be applied to observe the degree of oxidative modification of lignin. The following research revealed that the origin of AL is not some oxidized structure of lignin, but a certain wood extractives.

6. Concluding Remarks

Concluding Remarks

Chlorine bleaching of kraft pulp for paper making inevitably produce chloro-organics in the course of degradation and/or removal of lignin, one of the major wood components. On the surge of environmental concern and market pressure, pulp and paper industry in the West has been employing chlorine-free or chlorine-less bleaching process instead of the conventional chlorine bleaching technology. Pulp and paper industry in Japan, however, still uses chlorine-based bleaching sequences, and enormous amount of organic substances, some of which show acute or chronic toxity and mutagenicity due to organochlorine, are emitted to the environment. It is required quite urgently to establish a new evaluation method for the better understanding of the formation mechanism and to clarify the fate of these compounds in the ecosystem in the long period of time.

As far as its reactivity toward lignin is concerned, chlorine is known as one of the most effective bleaching agents. Systematic knowledge about the most important contributor to delignification during chlorine bleaching has yet to be established. Compiling a lot of information on chlorine chemistry leads to the better understanding of the feature of chloro-organics already deposited in the environment, as well as its contribution to modern science. Additionally, it will serve as a hint to the establishment of a new bleaching technology. Against these backgrounds mentioned above, the author tried to obtain some basic knowledge about the chemistry of the reaction between chlorine and lignin. The candidate quantitatively analyzed what is the main reaction caused by chlorine, and further investigated what reaction by chlorine contributes to delignification. The candidate also made attempts to analyze oxidized lignins and chloroform. The candidate tried to clarify the formation mechanism and/or the structural origin of those compounds. The important role of oxidation reaction by chlorine is always within the scope of the discussion over the whole story of this thesis.

It has been known from the early stage of bleaching chemistry that substitution reaction, oxidation reaction, and catalytic hydrolysis reaction by elemental chlorine are deeply related to the structural modification of lignin during chlorine bleaching of pulp. Few attempts, however, have been made so far to evaluate quantitatively how much these reactions contribute to the structural modification and removal of lignin during chlorine bleaching process. The candidate, focusing on the importance of oxidation reaction by chlorine, calculated the proportion of oxidation reaction and substitution reaction occurred in the course of chlorine bleaching, using pH-adjusted (High pH: oxidation-enhanced reaction condition) and pH-unadjusted (Low pH: oxidation-suppressed reaction condition) chlorine waters. The calculation is based on the amount of chloride produced during both chlorination and alkali treatment of kraft pulp, which is determined by ion chromatography. Kappa number of pulp, as an indication for the degree of delignification during bleaching, was also determined to see its relationship to the progress of oxidation reaction by chlorine. The result showed that 3.0 and 4.4 electrons were lost from one lignin structural unit, depending on whether chlorine oxidation was suppressed and enhanced, respectively. This explains the reason the oxidation-favorable reaction condition effectively removes lignin from kraft pulp. It also clarified that oxidation reaction proceeds to a substantial degree even under a reaction condition (using pH-unadjusted chlorine water) where substitution reaction is thought to occur predominantly. It is surprising that 4.4 electrons were abstracted from one lignin structural unit, though under oxidation-favorable reaction condition which is not applied to commercial use. Chlorine-free bleaching agents such as oxygen and hydrogen peroxide, which are being in wide use all over the world, can never achieve that degree of oxidation. It is thought that compared with other chlorine-free bleaching agents, chlorine can maintain pulp strength property because it does not produce active chemical species that attacks carbohydrates. Although chlorine may bring serious environmental impact, it can be said that chlorine is given priority over any other bleaching agent as far as its reactivity toward lignin is concerned.

Substantial degree of methanol liberation can be observed when chlorine reacts with kraft pulp residual lignin. It is known that methanol derives from methoxyl group of lignin aromatics, and that lignin aromatics are easily and rapidly oxidized by chlorine immediately after they lose methoxyl group. Methoxyl loss and methanol formation can, thus, be used as a promising indication for the degree of oxidized modification of pulp residual lignin. The candidate tried to investigate how reaction conditions of chlorination (i.e. pH and chlorine charge multiple) affect lignin degradation and delignification, using pH-adjusted and pH-unadjusted chlorine water. At a given chlorine multiple, methanol liberation was enhanced to a greater degree under oxidation-favorable reaction condition (High pH: using pH-adjusted chlorine water). Delignification was progressed more greatly under the condition than under oxidation-suppressed reaction condition. The results indicate that there is a strong relationship between methanol liberation and delignification, although the relationship can not be expressed as a single straight line. At a given degree of delignification, or kappa number reduction, there seems no significant difference between the two reaction conditions. Therefore, the progress of methanol liberation, or structural modification of lignin always seems to be accompanied by delignification. Relationship between kappa number and methoxyl content of bleached softwood kraft pulp was also investigated. Kappa number of CE-NKP was much lower than that of CW-NKP at a given chlorine charge multiple. These results suggest that part of pulp residual lignin is oxidized by chlorine treatment but can not be removed by water-washing, only to stay in CW-pulp. When oxidized portion of the lignin in CW-NKP is treated by warm alkali, it can be removed almost completely from the pulp to give CE-NKP. As a result of the quantitative removal of oxidized lignin, residual lignin in CE-NKP is thought to have aromatic character. Structural modification of aromatics, which leads to the release of methanol at high pH, causes the removal of lignin more effectively than that at low pH. Kappa number of both CW- and CE-NKPs by a certain chlorine dose was always lower for high pH condition than low pH condition. Since the high pH condition is more favorable to oxidation reaction, these results again confirm the importance of oxidation reaction for chlorine delignification.

Reduced emission of chloroform, known as one of the major volatile, low molecular weight chloro-organics produced in the chlorine bleaching process, is an urgent task for pulp and paper industry in Japan. Appropriate methods to evaluate chloroform formation are required, but chloroform is very difficult to determine accurately due to its high volatility and low aqueous solubility. The candidate tried to estimate possible chloroform formation, using a pressure-proof, gas tight reaction vessel to eliminate or minimize chloroform leakage into the air during both reaction and sampling. Softwood kraft pulp was chlorinated and treated by warm alkali in the sealed vessel to shift all chloroform produced in the process into the gas phase (headspace). Chloroform in the headspace gas was quantitatively determined by GC/MS with single ion monitoring to observe base ion peak of chloroform (m/z = 83 and 85). Chloroform formation increased with chlorine multiple, and substantial amounts of chloroform, most of which is present as its precursors, were seen to be produced by warm alkali treatment. Together with the additional experiment using MWL as a lignin model compound, it is strongly supported that possible chloroform formation per kappa number (lignin content) of pulp is almost constant for a given chlorine multiple, and that it is independent of kraft pulp with or without oxygen prebleaching. It is suggested that chloroform formation needs a certain degree of the progress of oxidation reaction. It is also suggested that there seems a certain threshold for chloroform to increase exponentially, regardless of the reaction condition of chlorination (pH of chlorine water). Although hypochlorite bleaching stage is by far the most contributor of chloroform production, it is indicated that comparable, even if not greater, amount of chloroform can be produced during both C- and E-stages when chloroform precursors are properly estimated.

Low molecular weight components of pulp bleaching effluent are relatively easy to analyze qualitatively and quantitatively, and numerous studies have so far been made on them. There seems virtually no analytical procedure established systematically for high molecular weight components of pulp bleaching effluent. Analytical methods frequently used in wood chemistry to investigate lignin structure are not applicable to the analysis of such high molecular weight compounds without pretreatment, because those components do not show aromatic character in spite of the fact that most of them have their origin in lignin aromatics. Analytical pyrolysis, or pyrolysis-gas chromatographic analysis often combined with mass spectrometry (Py-GC/MS), is thought to be one of the most promising methods for analysis of high molecular weight compounds. Relatively weak chemical bonding in high molecular compounds is easily cleaved instantaneously by the heat under a certain controlled condition of analytical pyrolysis, to yield low molecular weight compounds from which some information about the structure of the high molecular weight compounds can be obtained. Analytical pyrolysis has been successfully applied to the analysis of lignin preparations in the literature by other researchers. Chlorolignin isolated from chlorinated softwood kraft pulp and other oxidized lignin preparations, as well as extractives of unbleached pulp whose origin is assumed to be wood extractives, are analyzed by the candidate to investigate if analytical pyrolysis can also be applied to the analysis of high molecular weight components of chlorine bleaching effluent. A lot of low molecular weight aromatics (AR) were detected from lignin preparations such as MWL and kraft lignin by this method, as reported in the previous studies, while only small amount of them is detected from oxidized lignins. It was, however, observed that oxidized lignins gave a specific peak pattern on gas chromatogram (pyrogram). This is ascribed to a series of compounds carrying alkane-type structure (AL). Significant relationship between the degree of oxidation the oxidized lignin underwent and the peak area ratio of AL to AR (AL/AR) were observed, indicating the value AL/AR is a good indication for the structural modification of lignins prepared under some oxidizing condition of bleaching. It is concluded that analytical pyrolysis can be applied to observe the degree of oxidative modification of lignin. The following research revealed that the origin of AL is not some oxidized structure of lignin, but a certain wood extractives.

7. References

References for chapter 1

1. Yearbook of Paper and Pulp Statistics (1998) (in Jananese). complied by Research and Statistics Department, Minister's Secretariat, Ministry of International Trade and Industry: p.30
2. Yearbook of Paper and Pulp Statistics (1976) (in Jananese). complied by Research and Statistics Department, Minister's Secretariat, Ministry of International Trade and Industry: p.24
3. Rydholm SA (1965) Pulping Processes. Interscience Publishers: p.439-441, 576-578
4. Rydholm SA (1965) Pulping Processes. Interscience Publishers: p.839-841
5. Casey JP (editor) (1980) Pulp and Paper. Chemistry and Chemical Technology. A Wiley Interscience Publication (third edition), Volume I: p.634
6. Eero Sjöström (1981) Wood Chemistry. Fundamentals and Applications. Academic Press (1st edition): p.146
7. Dence CW, Reeve DW (editors) (1996) Pulp Bleaching Principles and Practice. Tappi Press: p.6
8. Walden CC and Howard TE (1981) Toxicity of Pulp and Paper Mill Effluents – a Review. Pulp and Paper Canada 82(4): T143-T146
9. Lalonde RT, Cook GP, Perakyla H, Dence CW, Babish JG (1991) Salmonella typhimurium (TA100) Mutagenity of 3-Chloro-4-(Dichloromethyl)-5-Hydroxy-2(5H)-Furanone and Its Open- and Closed Ring Analogs. Environmental and Molecular Mutagenesis 17: 40-48
10. Tachibana S, Santodonato J, Dence CW (1988) The Effect of Various Nucleophiles on the Mutagenicity of Softwood Kraft Chlorination Liquor. Chemosphere 17(7):

1343-1354

11. Ishiguro Y, Lalonde RT, Dence CW (1987) Mutagenicity of Chlorine-Substituted Furanones and Their Inactivation by Reaction with Nucleophile. Environmental Toxicology and Chemistry 6: 935-946
12. Lalonde RT, Perakyla H, Cook GP, Dence CW (1990) Contributio of the 5-Hydroxyl Group to the Mutagenicity of Mucochloric Acid. Environmental Toxicology and Chemistry 9: 687-691
13. Tachibana S, Santodonato J, Dence CW (1989) Reactions of Selected Nucleophiles with 2-Chloropropenal, a Mutagenic Constituent of Softwood Kraft Chlorination Effluent. Environmental Toxicology and Chemistry 8: 1133-1139
14. Lee EGH, Mueller JC, Walden CC Stich H (1981) Mutagenic Properties of Pulp Mill Effluents. Pulp and Paper Canada 82(5): T149-T154
15. Matsumoto Y (1989) The Present Issue of the Effluent from Chlorine Bleaching of Pulp. (in Japanese) Japanese Journal of Paper Technology 32(8): 7-11, 30
16. Matsumoto Y (1991) Pulp and Paper Industry and the Present Issue of Dioxine (in Japanese) Japanese Journal of Paper Technology 34(5): 53-59
17. Kringstad KP, Lindstrom K (1984) Spent Liquors from Pulp Bleaching. Environmental Science and Technology 18(8): 236A-248A
18. Umemoto K (1988) Inorganic Chemistry (in Japanese). Shokabo: 166-168
19. Eero Sjöström (1981) Wood Chemistry. Fundamentals and Applications. Academic Press (1st edition): p.148-150
20. Dence CW, Reeve DW (editors) (1996) Pulp Bleaching. Principles and Practice. Tappi Press: p.4-6, 73-77, 243-246
21. Hisey WO, Koon CM (1936) The Effect of pH on the Rate of Chlorine Consumption in Bleaching. Paper Trade Journal 103(6): 36-41

22. Sarkanen KV, Dence CW (1960) Reactions of p-Hydroxybenxyl Alcohol Derivatives and Their Methyl Ethers with Molecular Chlorine. Journal of Organic Chemistry 25: 715-720
23. Dence C, Sarkanen K (1960) A proposed Mechanism for the Acidic Chlorination of Softwood Lignin. Tappi 43(1): 87-96
24. Sarkanen KV, Strauss RW (1961) Demethylation of Lignin and Lignin Models by Aqueous Chlorine Solutions. I. Softwood Lignins. Tappi 44(7): 459-464
25. Van Buren JB, Dence CW (1967) Identification and Estimation of Primary Products from the Reactions of Chlorine with Lignin Model Compounds. Tappi 50(11): 553-560
26. Dence CW, Meyer JA, Unger K, Sadowski J (1965) Steric Effects in the Dealkylation of Phenol Ethers with Aqueous Chlorine. Tappi 48(3): 148-157
27. Van Buren JB, Dence CW (1970) Chlorination Behavior of Pine Kraft Lignin. Tappi 53(12): 2246-2253
28. Braddon SA, Dence CW (1968) Structure and Reactivity of Chlorolignin. I. Alkaline Hydrolysis of Chlorine-Substituted Lignin Model Compounds. Tappi 51(6): 249-256
29. Kempf AW, Dence CW (1970) Structure and Reactivity of Chlorolignin. II. Alkaline Hydrolysis of Chlorinated Kraft Pulp. Tappi 53(5): 864-873
30. Sato K, Kobayashi A, Mikawa H (1962) Chlorination of Guaiacol as a Model Compound of Benzene Nucleus of Lignin (in Japanese). Kamipa Gikyoshi 16(3): 180-190
31. Sato K, Kobayashi A, Mikawa H (1963) Chlorination of Barium Vanillyl Sulphonate Related to Mechanism of Pulp Bleaching (in Japanese). Kamipa Gikyoshi 17(7): 431-439

32. Kaneshige M, Takenaka H, Ito M, Kondo T (1962) Studies on Pulp Bleaching (I) Comparative Chlorination of Sulfite and Kraft Pulps (in Japanese). Kamipa Gikyoshi 16(6): 521-526

33. Terashima N, Shinoda Y, Kanda T (1974) Bleaching of Kraft Pulp with Chlorine I (in Japanese). Mokuzai Gakkaishi 20(10): 494-500

34. Shinoda Y, Terashima N, Kanda T (1974) Bleaching of Kraft Pulp with Chlorine II (in Japanese). Mokuzai Gakkaishi 20(10): 501-506

35. Shinoda Y, Kanno K, Kawamura I (1978) Bleaching of Kraft Pulp with Chlorine III. Effect of hemicellulose on the Formation of Coloring Materials of Low Bleachability (in Japanese). Mokuzai Gakkaishi 24(4): 250-255

36. Shinoda Y, Kanno K, Tajima T (1981) Bleaching of Kraft Pulp with Chlorine IV (in Japanese). Mokuzai Gakkaishi 27(4): 296-301

37. Kawachi S, Kondo T (1967) Studies on Pulp Bleaching (V) Significance of Chlorination and Alkali-Extraction on Pulp Bleaching (in Japanese). Kamipa Gikyoshi 21(9): 487-493

38. Kazuhiko Sameshima, Kondo T (1970) Studies on Pulp Bleaching (VII) On the Action Characteristics of Some Bleaching Chemicals and Its Significance in the Multistage Bleaching Practice (in Japanese). Kamipa Gikyoshi 24(1): 17-25

39. Kawachi S, Takei H (1969) Studies on Chlorination and Alkali-Extraction of Lignins. II. Solubilization of Dioxane Lignin on Chlorination and Alkali-Extraction (in Japanese). Mokuzai Gakkaishi 15(5): 222-227

40. Kawachi S, Takei H (1969) Studies on Chlorination and Alkali-Extraction of Lignins. III. Moisture Absorption Properties of Chlorinated Dioxane Lignins (in Japanese). Mokuzai Gakkaishi 15(5): 228-233

41. Kawachi S, Takei H (1975) Studies on Chlorination and Alkali-Extraction of

Lignins. IV. Chlorination of Dioxane Lignin in Homogeneous Media (in Japanese). Mokuzai Gakkaishi 21(8): 466-472

42. Kawachi S, Takei H (1977) Studies on Chlorination and Alkali-Extraction of Lignins. V. Consumption of Potassium Permanganate by Chlorinated Dioxane Lignin (in Japanese). Mokuzai Gakkaishi 23(5): 249-254
43. Kawachi S, Takei H (1969) Studies on Chlorination and Alkali-Extraction of Lignins. VI. Some Physico-Chemical Properties of Chlorinated Dioxane Lignins (in Japanese). Mokuzai Gakkaishi 23(10): 494-498
44. Remberger M, Hynning PÅ, Neilson AH (1990) Gas Chromatographic Analysis and Gas Chromatographic-Mass Spectrometric Identification of Components in the Cyclohexane-Extractable Fraction from Contaminated Sediment Samples. Journal of Chromatography 508: 159-178
45. Smith TJ, Wearne RH, Wallis FA (1994) An Ubiquitous Chlorohydroxypyrone in Filtrates from Chlorine Prebleaching of Alkaline Pulps. Holzforshing 48(5): 423-428
46. Juuti S, Vartiainen T, Ruuskanen J (1996) Formation of Organochlorine Compounds in Kraft Pulp Bleaching Processes. Chemosphere 33(12): 2431-2440
47. Neilson AH (1996) An Environmental Perspective on the Biodegradation of Organochlorine Xenobiotics. International Biodeterioration and Biodegradation: 3-21
48. Paasivirta J, Knuutinen J, Knuutila M, Maatela P, Pastinen O, Virkki L, Paukku R, Herve S (1988) Lignin and Organic Chlorine Compounds in Lake Water and the Role of the Chlorobleaching Effluents. Chemosphere 17(1): 147-158
49. Mori K (1988) Organic Chemistry II. The Chemistry of Functional Groups (in Japanese). Yokendo: p.96-98

50. Hrutfiord BF, Negri AR (1990) Chemistry of Chloroform Formation in Pulp Bleaching: a Review. Tappi Journal 73(6): 219-225
51. Rook JJ (1976) Haloforms in Drinking Water. Journal American Water Works Association 68(3): 168-172
52. Rook JJ (1977) Chlorination Reactions of Fulvic Acids in Natural Waters. Environmental Science and Technology 11(5): 478-482
53. Boyce SD, Horing JF (1983) Reaction Pathways of Trihalomethane Formation from the Halogenation of Dihydroxyaromatic Model Compounds for Humic Acid. Environmental Science and Technology 17(4): 202-210
54. Davison WHT, Slaney S, Wragg AL (1954) A Novel Method of Identification of Polymers. Chemistry and Industry 44: 1356
55. Kratzl K, Czepel H, Gratzl J (1965) Gaschromatographische Studien zur Pyrolyse des Lignins. Holz als Roh- und Werkstoff 23: 237-240
56. Kuroda K, Sakai K: Analysis of Lignin by Pyrolysis-Gas Chromatography II. Effect of Borosilicate Glass Fibers on Pyrolysis Product Composition (in Japanese). Mokuzai Gakkaishi 39(5): 584-589 (1993)
57. Kuroda K, Yamaguchi A, Sakai K (1994) Analysis of Sugi Wood and Its Lignin Preparations by Pyrolysis-Gas Chromatography (in Japanese). Mokuzai Gakkaishi 40(9): 987-995
58. Kuroda K, Suzuki A (1995) Analysis of Cinnamic Acids in Rice (*Oryza sativa*) by Simultaneous Pyrolysis-Methylation Gas Chromatography. Mokuzai Gakkaishi 41(9): 851-857
59. Suzuki S, Izumi A, Ohi H, Kuroda K, Yamaguchi A (1994) Structural Analysis of Alkaline Cooked Lignin by Pyrolysis-gas Chromatography. Evaluation of uniformity in Delignification of Beech Wood Chips (in Japanese). Kamipa

Gikyoshi 48(9): 1212-1220

60. Suzuki S, Izumi A, Ohi H, Kuroda K, Yamaguchi A (1995) Structural Analysis of Lignin by Pyrolysis-Gas Chromatography (II). Analysis of Decayed Wood Lignin (in Japanese). Kamipa Gikyoshi 49(4): 735-745
61. Izumi A, Ohi H, Kuroda K, Yamaguchi A (1995) Structural Analysis of Lignin by Pyrolysis-Gas Chromatography (III). Comparative Studies of Pyrolysis-Gas Chromatography and Nitrobenzene Oxidation for the Determination Method of Lignin Composition in Hardwood (in Japanese). Kamipa Gikyoshi 49(9): 1339-1346
62. Tanaka J, Izumi A, Suzuki S, Ohi H, Kuroda K (1997) Structural Analysis of Lignin by Pyrolysis-Gas Chromatography (IV). Comparison with Nitrobenzene Oxidation for Determination of Decayed Hardwoods and Kraft-Cooked Hardwoods (in Japanese). Kamipa Gikyoshi 51(2): 358-366
63. Izumi A, Kuroda K (1997) Pyrolysis-Gas Chromatography Analysis of Dehydro-Genation Polymers with Various Syringyl to Guaiacyl Ratios. Mokuzai Gakkaishi 43(2): 194-202
64. Izumi A, Kuroda K (1997) Pyrolysis-Mass Spectrometry Analysis of Dehydrogenation Lignin Polymers with Various Syringyl/Guaiacyl Ratios. Rapid Communications in Mass Spectrometry 11: 1709-1715
65. Faix O, Meier D, Fortmann I (1990) Thermal Degradation Products of Wood. Gas Chromatographic Separation and Mass Spectrometric Characterization of Monomeric Lignin Derived Products. Holz als Roh- und Werkstoff 48: 281-285
66. Faix O, Meier D, Fortmann I (1990) Thermal Degradation of Wood. A Collection of Electron-Impact (EI) Mass Spectra of Monomeric Lignin Derived Products. Holz als Roh- und Werkstoff 48: 351-354

67. Faix O, Fortmann I, Bremer J, Meier D (1991) Thermal Degradation Products of Wood. Gas Chromatographic Separation and Mass Spectrometric Characterization of Polysaccharide Derived Products. Holz als Roh- und Werkstoff 49: 213-219

68. Faix O, Fortmann I, Bremer J, Meier D (1991) Thermal Degradation of Wood. A Collection of Electron-Impact (EI) Mass Spectra of Polysaccharide Derived Products. Holz als Roh- und Werkstoff 49: 299-304

69. Faix O, Meier D, Grobe I (1987) Studies on Isolated Lignins and Lignins in Woody Materials by Pyrolysis-Gas Chromatography-Mass Spectrometry and Off-line Pyrolysis-Gas Chromatography with Flame Ionization Detection. Journal of Analytical and Applied Pyrolysis 11: 403-416

70. Salo S, Niemelä S, Elomaa M, Lindberg JJ (1989) Identification of Lignins by Pyrolytical Methods. Holzforshung 43(4): 257-260

71. Kleen M, Gellerstedt G (1991) Characterization of Chemical and Mechanical Pulps by Pyrolysis-Gas Chromatography/Mass Spectrometry. Journal of Analytical and Applied Pyrolysis 19: 139-152

72. Van Loon WMGM, Boon JJ, De Groot B (1991) Qualitative Analysis of Chlorolignins and Lignosulphonates in Pulp Mill Effluents Entering the River Rhine Using Pyrolysis-Mass Spectrometry and Pyrolysis-Gas Chromatography /Mass Spectrometry. Journal of Analytical and Applied Pyrolysis 20: 275-302

73. Sasaki N, Suzuki M, Sakata K, Nagasawa T (1986) Pyrolysis of Lignins and Related Compounds I. Pyrolysis of Chlorinated Phenolic Compounds. Mokuzai Gakkaishi 32(4): 255-260

74. Sasaki N, Suzuki M, Sakata K, Nagasawa T (1986) Pyrolysis of Lignins and Related Compounds II. Pyrolysis of Chlorinated Thiolignin. Mokuzai Gakkaishi 32(4): 261-265

75. Shimada K (1977) Organic Compounds in Kraft Bleaching Spent Liquor. II. Alkaline Cupric Oxide Oxidation of Red Pine Chlorinated Oxylignin. Mokuzai Gakkaishi 23(5): 243-248
76. Shimada K (1980) Organic Compounds in Kraft Bleaching Spent Liquors III. Chlorinated Aromatic Compounds in Beech Kraft Bleach Effluents. Mokuzai Gakkaishi 26(8): 543-551
77. Shimada K (1981) Organic Compounds in Kraft Bleaching Spent Liquors IV. Toxicity Bioassay of Organic Compounds from Beech Kraft Bleach Effluents. Mokuzai Gakkaishi 27(6): 470-477
78. Shimada K (1982) Organic Compounds in Kraft Bleaching Spent Liquors V. Phtodegradation of Red-Pine Chlorinated Oxilignin. Mokuzai Gakkaishi 28(6): 376-382

References for chapter 2

1. Rydholm SA (1965) Pulping Processes, Interscience Publishers: p.916-939
2. Giertz HW (1951) Developments in Bleaching Processes. Tappi 34(5): 209-215
3. Grangaard DH (1956) Bleaching I. The Chlorination of Pulp. Tappi 39(5): 270-276
4. Tabei K, Kaneko Y, Akiyama T, Ueno T (1980) Studies on Bleaching of Pulps Part 1. The Oxidation Reaction and the Substitution Reaction in Chlorine Treatment (in Japanese). Kamipa Gikyoshi. 34(9): 621-628
5. Shintani H, Matsumoto Y, Ishizu A, Meshitsuka G (1994) Formation Characteristics of Chloroorganics from Hardwood Kraft Pulp during Chlorine Bleaching. Sen'i Gakkaishi 50(12): 587-592
6. Migita N, Nakano J, Ishizu A (1955) Studies on Lignin. XXIV. On the Chlorination of Lignin (in Japanese). Mokuzai Gakkaishi 1(2): 55-59
7. Shintani H, Matsumoto Y, Meshitsuka G (1996) The Unsuitability of AOX as a Measure of the Organic Chlorine Content of C-stage Effluents. Journal of Pulp and Paper Science 22(10): J372-J375
8. Shintani H, Matsumoto Y, Meshitsuka G (1995) Structure of High Molecular Weight Chlorolignin Produced by Chlorine Bleaching. Proceedings of 8th International Symposium on Wood and Pulping Chemistry, Helsinki, June 1995, Volume II: 309-314

References for chapter 3

1. Shintani H, Matsumoto Y, Ishizu A, Meshitsuka G (1994) Formation Characteristics of Chloro-organics from Hardwood Kraft Pulp during Chlorine Bleaching. Sen'i Gakkaishi 50(12): 587-592
2. Sporek KF, Danyi MD (1962) Detection and Identification of Alcohols, Alkoxy Groups, Lignin, and Wood by Gas Liquid Chromatography. Analytical Chemistry 34(12): 1527-1529
3. White EV, Swartz JN, Peniston QP, Schwartz H, McCarthy JL, Hibbert H (1941) Mechanism of the Chlorination of Lignin. Technical Association Papers 24(1): 179-189
4. Sarkanen KV, Strauss RW (1961) Demethylation of Lignin and Lignin Models by Aqueous Chlorine Solutions I. Softwood Lignins. Tappi 44(7): 459-464
5. Ivancic A, Rydholm SA (1959) Technical Color Reactions of Lignin. Svensk Papperstidning 62(16): 554-566
6. Ni Y, Kubes GJ, Van Heiningen ARP (1990) A New Mechanism for Pulp Delignification During Chlorination. Journal of Pulp and Paper Science 16(1): J13-J19
7. Ni Y, Kubes GJ, Van Heiningen ARP (1990) Methanol Number: A New Method to Determine Lignin Content of Pulp. Journal of Pulp and Paper Science 16(3): J83-J86
8. Hosoya S (1992) Non-Chlorine Bleaching in View of Structures and Reactions of Residual Lignin in Kraft Pulp (in Japanese). Kamipa Gikyoshi. 46(11): 1344-1361
9. Hosoya S, Taneda H, Chang HM (1989) Formations and Reactions of Ether-Type Lignin Carbohydrate Complex. Proceedings of the 5th International Symposium on

Wood and Paper Chemistry, Raleigh, NC, May 1989: 69-73

10. Shintani H, Matsumoto Y, Meshitsuka G (1995) Structure of High Molecular Weight Chlorolignin Produced by Chlorine Bleaching. Proceedings of 8th International Symposium on Wood and Pulping Chemistry, Helsinki, June 1995, Volume II: 309-314
11. Tong G, Matsumoto Y, Meshitsuka G (2000) Analysis of Progress of Oxidation Reaction during Oxygen-Alkali Treatment of Lignin. II. The Significance of Oxidation Reaction of Lignin during Oxygen Deligninfication. Journal of Wood Science (in press)

References for chapter 4

1. Crawford RJ, Stryker MN, Jett SW, Carpenter WL, Fisher RP, Jain AK (1987) Laboratory Studies of Chloroform Formation in Pulp Bleaching. Tappi Journal 70(11): 123-128
2. Crawford RJ, Stryker MN (1988) Factors That Affect the Generation of Chloroform in Bleaching. Tappi Journal 71(11): 151-159
3. Magara K, Hosoya S, Tomimura Y (2000) Degradation of Chloroform Produced during Pulp Bleaching. Abstracts of the 50th Annual Meetings of the Japan Wood Research Society (Wood 2000 Kyoto), Kyoto: 333
4. Uchiyama K (1998) Voluntary Control Plan on Hazardous Air Pollutant (Chloroform) (in Japanese). Kamipa Gikyoshi 52(5): 588-594
5. Kaiser KLE, Oliver BG (1976) Determination of Volatile Halogenated Hydrocarbons in Water by Gas Chromatography. Analytical Chemistry 48(14): 2207-2209
6. Dietz, Jr EA, Singley KF (1979) Determination of Chlorinated Hydrocarbons in Water by Headspace Gas Chromatography. Analytical Chemistry 51(11): 1809-1814
7. Friant SL, Suffet IH (1979) Interactive Effects of Temperature, Salt Concentration, and pH on Head Space Analysis for Isolating Volatile Trace Organics in Aqueous Environmental Samples. Analytical Chemistry 51(13): 2167-2172
8. Chai XS, Dhasmana B, Zhu JY (1998) Determination of Volatile Organic Compound Contents in Kraft Mill Streams Using Headspace Gas Chromatography. Journal of Pulp and Paper Science 24(2): 50-54
9. Koshitsuka T (1998) New Application of Hydrogen Peroxide in Chemical Pulp

Bleaching (in Japanese). Kamipa Gikyoshi 52(5): 623-629

10. Björkman A (1956) Studies on Finely Divided Wood. Part 1. Extraction of Lignin with Neutral Solvents. Svensk Papperstidning 59: 477-485
11. Crawford RJ, Dallons VJ, Jain AK, Jett SW (1991) Chloroform Generation at Bleach Plants with High Chlorine Dioxide Substitution or Oxygen Delignification. Tappi Journal 74(4): 159-163
12. Iimori T, Iwase Y, Tsuji Y (1999) Effect of Bleaching Conditions on Chloroform Generation (in Japanese). Kamipa Gikyoshi 53(10): 1356-1362
13. Rydholm SA (1965) Pulping Processes. International Publishers, 919-921
14. Dence CW, Reeve DW (1996) Pulp Bleaching Principles and Practice. Tappi Press, 245-247
15. Dallons VJ, Hoy DR, Messmer RA, Crawford RJ (1990) Chloroform Formation and Release from Pulp Bleaching. Results of Field Measurements. Tappi Journal 73(6): 91-95

References for chapter 5

1. Kuroda K, Sakai K (1993) Analysis of Lignin by Pyrolysis-Gas Chromatography II. Effect of Borosilicate Glass Fibers on Pyrolysis Product Composition (in Japanese). Mokuzai Gakkaishi 39(5): 584-589
2. Kuroda K, Yamaguchi A, Sakai K (1994) Analysis of Sugi Wood and Its Lignin Preparations by Pyrolysis-Gas Chromatography (in Japanese). Mokuzai Gakkaishi 40(9): 987-995
3. Kuroda K, Suzuki A (1995) Analysis of Cinnamic Acids in Rice (*Oryza sativa*) by Simultaneous Pyrolysis-Methylation Gas Chromatography. Mokuzai Gakkaishi 41(9): 851-857
4. Suzuki S, Izumi A, Ohi H, Kuroda K, Yamaguchi A (1994) Structural Analysis of Alkaline Cooked Lignin by Pyrolysis-Gas Chromatography. Evaluation of Uniformity in Delignification of Beech Wood Chips (in Japanese). Kamipa Gikyoshi 48(9): 1212-1220
5. Suzuki S, Izumi A, Ohi H, Kuroda K, Yamaguchi A (1995) Structural Analysis of Lignin by Pyrolysis-Gas Chromatography (II). Analysis of Decayed Wood Lignin (in Japanese). Kamipa Gikyoshi 49(4): 735-745
6. Izumi A, Ohi H, Kuroda K, Yamaguchi A (1995) Structural Analysis of Lignin by Pyrolysis-Gas Chromatography (III). Comparative Studies of Pyrolysis-Gas Chromatography and Nitrobenzene Oxidation for the Determination Method of Lignin Composition in Hardwood (in Japanese). Kamipa Gikyoshi 49(9): 1339-1346
7. Tanaka J, Izumi A, Suzuki S, Ohi H, Kuroda K (1997) Structural Analysis of Lignin by Pyrolysis-Gas Chromatography (IV). Comparison with Nitrobenzene

Oxidation for Determination of Decayed Hardwoods and Kraft-Cooked Hardwoods (in Japanese). Kamipa Gikyoshi 51(2): 358-366

8. Izumi A, Kuroda K (1997) Pyrolysis-Gas Chromatography Analysis of Dehydrogenation Polymers with Various Syringyl to Guaiacyl Ratios. Mokuzai Gakkaishi 43(2): 194-202
9. Izumi A, Kuroda K: Pyrolysis-Mass Spectrometry Analysis of Dehydrogenation Lignin Polymers with Various Syringyl/Guaiacyl Ratios. Rapid Communications in Mass Spectrometry 11: 1709-1715 (1997)
10. Faix O, Meier D, Fortmann I (1990) Thermal Degradation Products of Wood. Gas Chromatographic Separation and Mass Spectrometric Characterization of Monomeric Lignin Derived Products. Holz als Roh- und Werkstoff 48: 281-285
11. Faix O, Meier D, Fortmann I (1990) Thermal Degradation of Wood. A Collection of Electron-Impact (EI) Mass Spectra of Monomeric Lignin Derived Products. Holz als Roh- und Werkstoff 48: 351-354
12. Faix O, Fortmann I, Bremer J, Meier D (1991) Thermal Degradation Products of Wood. Gas Chromatographic Separation and Mass Spectrometric Characterization of Polysaccharide Derived Products. Holz als Roh- und Werkstoff 49: 213-219
13. Faix O, Meier D (1991) Thermal Degradation of Wood. A Collection of Electron-Impact (EI) Mass Spectra of Polysaccharide Derived Products. Holz als Roh- und Werkstoff 49: 299-304
14. Shintani H, Matsumoto Y, Ishizu A, Meshitsuka G (1994) Formation Characteristics of Chloro-organics from Hardwood Kraft Pulp during Chlorine Bleaching. Sen'i Gakkaishi 50(12): 587-592
15. Tong G, Yokoyama T, Matsumoto Y, Meshitsuka G (2000) Analysis of Progress of Oxidation Reaction during Oxygen-Alkali Treatment of Lignin I. Method and Its

Application to Lignin Oxidation. Journal of Wood Science 46(1): 32-39

16. Froass P, Ragauskas A, McDonough T, Jiang J (1996) Relationship between Residual Lignin Structure and Pulp Bleachability. Proceedings of 1996 International Pulp Bleaching Conference, Washington, D.C., April 1996, Book 1: 163-170
17. Björkman A (1956) Studies on Finely Divided Wood. Part 1. Extraction of Lignin with Neutral Solvents. Svensk Papperstidning 59: 477-485
18. Kuroda K, Yamaguchi A (1994) Classification of Japanese Softwood Species by Pyrolysis-Gas Chromatography. Journal of Analytical Pyrolysis 33: 51-59
19. Silverstein RM, Bassler GC, Morrill TC (1981) Spectrometric Identification of Organic Compounds (4th edition). John Wiley & Sons, Inc.: pp. 16-17
20. Shintani H, Matsumoto Y, Meshitsuka G (1995) Structure of High Molecular Weight Chlorolignin Produced by Chlorine Bleaching: Proceedings of the 8th International Symposium on Wood and Pulping Chemistry, Helsinki, June 1995, Volume II: 309-314
21. Van Loon WMGM, Boon JJ, De Groot B (1991) Qualitative Analysis of Chlorolignins and Lignosulphonates in Pulp Mill Effluents Entering the River Rhine Using Pyrolysis-Mass Spectrometry and Pyrolysis-Gas Chromatography / Mass Spectrometry. Journal of Analytical and Applied Pyrolysis 20: 275-302
22. del Río JC, Gutiérrez A, González-Vila FJ (1999) Analysis of Impurities Occurring in a Totally Chlorine Free-Bleached Kraft Pulp. Journal of Chromatography A, 830 (1): 227-232
23. del Río JC, Gutiérrez A, González-Vila FJ, Romero FMJ (1998) Characterization of Organic Deposits Produced in the Kraft Pulping of *Eucalyptus globulus* Wood. Journal of Chromatography A, 823 (1-2): 457-465

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List of Papers

1) Koda K, Shintani H, Matsumoto Y, Meshitsuka G (1999) Evaluation of the Extent of the Oxidation Reaction during Chlorine Bleaching of Pulp. Journal of Wood Science, 45(2): 149-153

2) Koda K, Shintani H, Matsumoto Y, Meshitsuka G (2000) Quantitative Study on the Possible Formation of Chloroform during Chlorine Bleaching of Kraft Pulp. (submitted to Journal of Wood Science)

3) Koda K, Goto H, Shintani H, Matsumoto Y, Meshitsuka G (2000) Oxidative Cleavage of Lignin Aromatics during Chlorine Bleaching of Kraft Pulp. (submitted to Journal of Wood Science)

4) Koda K, Shintani H, Matsumoto Y, Meshitsuka G (2000) Origin of Alkane-Type Structure Detected by the Analytical Pyrolysis of Oxidized Lignins. (will be submitted to Journal of Wood Science)

List of International Conferences

1) Shintani H, Koda K, Matsumoto Y, Meshitsuka G (1997) Resistance of Highly Chlorinated Lignin in Pulp toward Chlorine Oxidation. Proceedings of the 9th International Symposium on Wood and Pulping Chemistry, Montreal, June 1997 (poster presentation): 104-1 - 104-4

2) Koda K, Shintani H, Matsumoto Y, Meshitsuka G (1998) Environmental Fate of High Molecular Weight Chloroorganics Produced by Chlorine Bleaching (1). Development of a New Analytical Method by the Use of Pyrolysis Gas Chromatography. Proceedings of the 1998 International Pulp Bleaching Conference, Helsinki, June 1998, Book 2 (poster presentations): 609-612

3) Koda K, Shintani H, Matsumoto Y, Meshitsuka G (1999) Additional Evidences for the Dominance of Oxidation Reaction over Substitution Reaction during Chlorine Bleaching of Pulp" Proceedings of the 10th International Symposium on Wood and Pulping Chemistry, Yokohama, June 1999 Volume II (poster presentations): 306-311