



Sorption of organics from Kraft bleach wastewater  
by Robert Lindsay Anderson

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE in Civil Engineering  
Montana State University  
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**Abstract:**

The Kraft industry is responsible for large quantities of waste-water. This wastewater is characterized by its high color, BOD, suspended solids, and possible toxicity. Of these parameters, color is perhaps the most difficult to remove and has been the object of intensive research in the last decade.

The massive-lime process is capable of removing the bulk of the color from Kraft bleach wastewater. With the addition of sedimentation, biological oxidation, activated carbon sorption, and perhaps demineralization, a reusable water can be produced.

One of the objects of this research was to find a sorbent which, because of better performance or local availability, could replace activated carbon in the sorption step of the flow sheet. Several sorbents, including hog fuel ash, fly ash, diatomaceous earth, coal, bentonite, activated carbon, two filter aids, and three resins, were tested in batch processes after massive-lime reduction of color to 300 CU. Each wastewater was examined for color, TOC, and absorbance at 265 mu. Results showed that activated carbon and two resins, A-6 and S-37, performed best, producing a water which approached standards for bleached Kraft process water. Of the local sorbents, hog fuel ash was best. This sorbent, available at most Kraft mills, must be studied in a continuous flow process to determine its feasibility.

The second object of the research was to characterize the raw and treated wastewaters with respect to molecular size in order to determine the effect of molecular size on sorption. The raw and treated wastewaters were fractionated by gel permeation chromatography on Sephadex gels. GPC on Sephadex G-10 fractionated the samples into three fractions, all of molecular sizes less than 500 MW. There was no attempt to identify the three fractions.

That all fractionated molecules were of a size less than MW 500 confirmed reports that lime precipitation removes larger molecules.

The ratio of TOC applied/TOC eluate was different for each sample. This inconsistency could not be explained by the effects of pH and aromaticity.

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Date March 8, 1972

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FROM KRAFT BLEACH WASTEWATER

by

ROBERT LINDSAY ANDERSON

A thesis submitted to the Graduate Faculty in partial  
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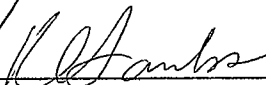
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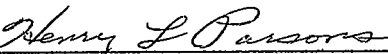
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Civil Engineering

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## ABSTRACT

The Kraft industry is responsible for large quantities of wastewater. This wastewater is characterized by its high color, BOD, suspended solids, and possible toxicity. Of these parameters, color is perhaps the most difficult to remove and has been the object of intensive research in the last decade.

The massive-lime process is capable of removing the bulk of the color from Kraft bleach wastewater. With the addition of sedimentation, biological oxidation, activated carbon sorption, and perhaps demineralization, a reusable water can be produced.

One of the objects of this research was to find a sorbent which, because of better performance or local availability, could replace activated carbon in the sorption step of the flow sheet. Several sorbents, including hog fuel ash, fly ash, diatomaceous earth, coal, bentonite, activated carbon, two filter aids, and three resins, were tested in batch processes after massive-lime reduction of color to 300 CU. Each wastewater was examined for color, TOC, and absorbance at 265 mu. Results showed that activated carbon and two resins, A-6 and S-37, performed best, producing a water which approached standards for bleached Kraft process water. Of the local sorbents, hog fuel ash was best. This sorbent, available at most Kraft mills, must be studied in a continuous flow process to determine its feasibility.

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That all fractionated molecules were of a size less than MW 500 confirmed reports that lime precipitation removes larger molecules.

The ratio of TOC applied/TOC eluate was different for each sample. This inconsistency could not be explained by the effects of pH and aromaticity.

## CHAPTER I

### INTRODUCTION

The pulp and paper industry is the fifth largest industry in the United States (32, 90) and is estimated to use over 2,100 billion gallons of water annually (13, 91).

Sixty percent of the pulp produced in the United States is manufactured by the Kraft (sulfate) process (13). Though this process recycles the water and chemicals which are used for pulping, the water used for make-up and for washing and bleaching the pulp averages 33,000 gallons per ton of product pulp (96). This large usage results in a significant wastewater pollution problem. This thesis investigates one aspect of this problem.

#### A. THE KRAFT PROCESS

In the Kraft process, which has been in use since before the year 1900, wood is cooked for four to twelve hours at temperatures from 165 - 175°C in a solution of sodium hydroxide and sodium sulfide. The result is wood pulp, with about eighty percent of the lignin removed (60), and a solution of degraded lignin and spent chemicals. This solution is known as "black liquor" and is processed for the recovery of chemicals.

##### 1. Bleaching

Pulp from Kraft cooking has high mechanical strength (Kraft is a German word for strong), but it also may be dark because of the

residues of lignin degradation and other products. Kraft pulp may undergo a series of washing and bleaching processes which oxidize and dissolve these residues (66, 69). The result is a strong pulp and large volumes of highly colored wastewater. The wastewater is the source of a pollution problem toward which this research was directed.

## 2. Hoerner Waldorf Kraft Mill

The Hoerner Waldorf Corporation pulp plant is located at Frenchtown, eighteen miles NW of Missoula, Montana, and 236 miles from Bozeman, Montana. The plant, which is considered to be of "medium" size, was constructed in 1957 and was expanded in 1960 to a daily production of 450 tons/day of Kraft paperboard and 150 tons/day of bleached Kraft pulp. Unbleached pulp production increased to 900 tons/day in 1966 (74).

The bleaching process at Hoerner Waldorf consists of four stages: 1) chlorination, 2) caustic extraction, 3) sodium hypochlorite, and 4) chlorine dioxide. Each stage is followed by washing. Due to extensive countercurrent water reuse, the wastewater flows from these processes consist of about 3000 gpm from the chlorination washer, 450 gpm from the caustic washer, and small sporadic flows from spills, leakage and wash-down operations (74).

Since this Kraft mill and its bleaching processes are considered "typical", research on its wastewater pollution problems is not only significant from a local viewpoint, but also from one which is nation-wide.

## B. WASTEWATER POLLUTION PROBLEMS FROM KRAFT BLEACH MILLS

Wastewater pollution problems associated with Kraft bleach mills may be classified with respect to four general pollutants:

1. Suspended solids
2. Biochemical oxygen demand (BOD)
3. Color
4. Toxicity

### 1. Suspended Solids

Suspended solid matter in Kraft bleach wastewater, which includes fibers and other dispersed insoluble wood components and process chemicals, can form bottom deposits in receiving streams. These deposits can be unsightly, odiferous, and deleterious to aquatic life (32, 34). On decomposition, they contribute to biochemical oxygen demand.

### 2. Biochemical Oxygen Demand

Two of the major dissolved organic components of Kraft bleach wastewater are lignin degradation products and carbohydrates. Lignins and lignin degradation products biodegrade very slowly and therefore contribute only slightly to BOD. Carbohydrates, such as wood sugars, on the other hand, are readily assimilated by a variety of microorganisms, and exert a significant demand on the dissolved oxygen of a stream (13, 32, 34, 60). Oxygen demanding materials also promote the growth of slime organisms on stream bottoms (34).

### 3. Color

In the Kraft process, a significant amount of the highly colored lignin degradation products remain attached to the cellulose fibers. The bleaching process transfers much of this colored matter from the fibers to the process water. The result is a highly colored wastewater (7, 11, 14, 21, 84).

Early pulp and paper industry spokesmen held that color, per se, was not a pollutant. However, it was recognized that color had an adverse psychological and aesthetic effect (11, 30, 40, 60), and that the industry was responsible for reducing it to acceptable levels. More recently, color has been criticized also for its pollutional effects (84):

1. Color may reduce sunlight penetration into water and inhibit the growth of desirable aquatic plants.
2. Colored components may be toxic to aquatic organisms.
3. Color may require removal before a water can be used as a potable supply or for certain industrial processes, including the Kraft process.

Furthermore, water quality regulatory agencies are becoming less tolerant of any organic material in effluents. For all of these reasons, color is now recognized as the major wastewater problem facing the Kraft industry (63).

#### 4. Toxicity

The toxic effects of the colored components of Kraft bleach wastewater have been the subject of disagreement, mostly because of a dearth of research on the subject.

Howard and Walden (42) reported that salmonid fishes were adversely affected by Kraft effluents, but that they became acclimated, and that the effects were due mostly to pH. These authors later devised a technique which showed the toxicity of effluents to be independent of pH. Their tests showed that the test organisms (young salmon) had a Medium Survival Time (MST) of 136 minutes in 100 percent caustic extract (41).

Sprague and Drury (83) determined that salmon showed moderate avoidance to concentrations of Kraft bleach wastewater varying from 10 ppm to 10 percent.

Walden, et al (95), found that fish respiration was noticeably affected by a four percent concentration of Kraft bleach wastewater.

There is no evidence that this toxicity is due to the colored components. The question will likely never be answered because of the recognition of color as a pollutant on other grounds, because of concerted efforts on the part of the industry to remove color, and because of the difficulty of separating the colored components from the other molecules in the wastewater.

## 5. Wastewater Reuse

Partly because of pollution control regulations, the Kraft bleach industry already recycles much of its process water. Added advantages to water reuse are savings in heat, fiber, chemicals, and the water itself (13, 32). As wastewater pollution standards become stricter, as water treatment costs rise, and as wastewater treatment technology improves, recycling of wastewater will increase. Ultimately, it seems likely that many industries, including the Kraft industry, will recycle all wastewater.

Process water used in the Kraft bleach process must meet certain quality criteria in order to maintain the quality of the pulp. Table 1 shows the ranges of desired properties for process water used in both the unbleached and bleached Kraft processes (57, 98). The most important of these properties with respect to Kraft bleach wastewater reuse are color (0-5 units), pH (6.8-7.3), dissolved solids (50-250 ppm), chloride (10-150 ppm), and chemical oxygen demand (0-8 ppm). It must be remembered, however, that the properties listed are ideals and that thousands of tons of Kraft pulp are being manufactured daily with waters that fail to meet these criteria (80, 89).

Chloride concentration has not previously been mentioned as a pollutant. It appears in high concentrations in bleach wastewaters and is important mostly from the standpoint of corrosiveness of recycled water (81).



TABLE 1

RANGES OF DESIRED PROPERTIES OF PROCESS WATER  
FOR KRAFT MANUFACTURE

<u>Property</u>	<u>Unbleached</u>	<u>Bleached</u>
Turbidity, units	5-25	0-5
Color, units	10-80	0-5
pH	6.5-8.0	6.8-7.3
Total Alkalinity, ppm	20-150	20-75
Hardness, ppm as CaCO <sub>3</sub>	5-200	5-100
Dissolved Solids, ppm	50-500	50-250
Chloride, ppm	10-150	10-150
Fe, ppm	<0.5	<0.2
Mn, ppm	<0.3	<0.1
COD, ppm	0-12	0-8
BOD, ppm	0-5	0-2

A water which meets the criteria for bleached Kraft process water as listed in Table 1 may also be suitable for potable water supply. Though potable water must meet a number of criteria not applicable to bleached Kraft process water, several criteria are common to both. Table 2 lists these common criteria as proposed by the U.S. Public Health Service for potable water (92). It may be seen that, with respect to these criteria, bleached Kraft process water standards compare favorably with potable water standards.

TABLE 2

## POTABLE WATER STANDARDS

<u>Property</u>	<u>Concentration Limit</u>
Turbidity, units	5
Color, units	15
Total dissolved solids, mg/l	500
Chloride, mg/l	250
Fe, mg/l	0.3
Mn, mg/l	0.03

C. STATEMENT OF THE PROBLEM

Laboratory and pilot plant investigations at the Southern Research Center of the National Council of the Paper Industry for Air and Stream Improvement (NCASI) by Berger, et al (8, 81, 88, 89), have shown that Kraft process wastewaters may be treated in a step by step process to yield a water that is completely reusable in Kraft pulp manufacture. The unit processes used are settleable solids removal, massive lime precipitation, aerobic biological oxidation, activated carbon adsorption, and demineralization.

Settleable solids are removed by plain sedimentation. This process removes seventy to ninety percent of the suspended solids; over ninety-five percent of the settleable solids, and about fifteen percent of the five-day BOD (34, 88).

Massive lime treatment, the key step in the flow sheet, is

capable of removing ninety percent of the color and fifty-five percent of the five-day BOD. The effluent of this process has a pH of about 11.0, so neutralization is required to precipitate lime from the saturated solution and to yield a water that is amenable to biological oxidation (88).

After lime treatment, up to ninety-five percent of the five-day BOD may be removed by one of a number of biological oxidation processes including oxidation ponds, activated sludge or trickling filters (34, 88).

Activated carbon adsorption is used as a polishing process which may reduce five-day BOD, color, COD and turbidity to levels below ten ppm (88).

Effluents from the Kraft bleaching process are high (up to 4000 mg/l) in concentrations of chloride. Several processes such as ion exchange, reverse osmosis, or electrodialysis can be used to reduce the chloride concentration to levels which prevent corrosion and enable wastewater recycling (88).

#### 1. Adsorption

Adsorption is the phenomenon whereby molecules adhere to a surface. If there is a chemical interaction between the molecules or particles in the fluid medium and the molecules or groups on the surface, then the process is called chemical adsorption or chemisorption. This type of adsorption involves strong bonding and is essentially irreversible (39, 47, 60, 62).

Contrasted to chemisorption is physical adsorption. In this process there is no chemical interaction. The bonding between the solute molecules and the surface is due to van der Waal's forces and is relatively weak and reversible. Physical adsorption is the type which reduces the concentrations of dilute solutions of organic molecules in water and wastewater treatment. This process allows for regeneration or reactivation and reuse of the adsorbent (39, 47, 60, 62).

A process closely related to adsorption is ion exchange. In this process, a solute molecule or ion is attached to a surface at a site previously occupied by another molecule or ion. The binding results from the greater affinity of the site for the solute molecule or ion than for the molecule or ion originally on the site. When it is not clear whether the solute molecule adheres through adsorption or ion exchange, or both, the general term "sorption" is often used.

In this thesis, the term sorption is used generally to mean physical adsorption, but use of the term will not imply that the mode of mechanism or the adherence is understood, nor that the adherence does not involve ion exchange.

The classic sorbent is activated carbon (activated charcoal). This material has been used for centuries for water purification, but the mechanisms and kinetics of the process are not yet completely understood (39, 47). Activated carbon generally refers to a carbon whose sorptive properties have been purposefully increased by man-made

operations. Activated carbon is manufactured from a number of materials including wood, coal, bone, nut shells, peat and petroleum base residues. Mostly because of the large surface area of activated carbon, up to 2500 square meters per gram, this material can sorb over ten percent of its weight of sorbate. Because of this effectiveness, activated carbon is widely used in water and wastewater treatment.

## 2. Other Sorbents

Despite its effectiveness, the use of activated carbon is limited by its cost. The first phase of this research was directed at investigating the sorptive properties of a number of other sorbents which might be more economical than activated carbon because of greater effectiveness or because of ready availability in Montana or in the Rocky Mountain area. The sorbents tested were local sorbents, filter aids, and resins.

Local sorbents were alumina, fly ash, bentonite, coal, and hog fuel ash. Alumina (aluminum oxide) is used as the raw material by the Anaconda Company aluminum reduction plant at Columbia Falls, Montana. Conceivably, the alumina could be used as a sorbent at Hoerner Waldorf and then shipped to Columbia Falls. The alumina could still be reduced to aluminum; the sorbate would be oxidized in the process.

Fly ash is the residue from coal combustion at steam power generating plants. It is available in large quantities throughout the United States (10). The Montana Power Company steam generating plant at Billings, Montana produces from seventy to 180 tons/day and

has a two-year supply on hand (64). If the fly ash could not be reactivated after sorption, it would have the disadvantage of presenting the same solid waste disposal problem it does now.

Bentonite is an aluminum silicate clay found in the Rocky Mountain area, particularly Wyoming, which forms a viscous gel with water. It could also present a solid waste disposal problem if regeneration proved difficult.

Coal is readily available throughout the Intermountain West. If successful as a sorbent, it would have the advantage of its utility as a fuel afterwards.

Hog fuel ash is the ash which remains after bark and rejected chips are burned as fuel at pulp mills. Large quantities are available at most mills. The Hoerner Waldorf mill produces about seven tons per day and has about 2500 tons on hand (101).

Filter aids which were tested were diatomaceous earth and two products marketed by Johns-Manville Corporation, Celkate and HyfloSupercel. All of these could present a sludge disposal problem.

Resins are synthetic organic polymers which may also aid in ion exchange demineralization. Those tested were Duolite resins A-6, S-37 and LAD-500.

Activated carbon was used as a standard for comparison with all other sorbents.

### 3. Artificial Ditch Waste

Wastewaters from the Hoerner Waldorf plant are collected in four

ditches. Ditch 1 carries wastewater from the clear water chest in the paper mill plus fresh water overflow. Ditch 2 carries wastewater from the floor drains, evaporators, the Kamyrr operation, and the recovery process in the pulp plant. Ditch 3 carries all of the wastewater from the bleaching operation plus leakage and wash water from the bleach, recausticizer, and kiln areas, possibly some black liquor, and paper machine waste (73, 74). This is the wastewater of primary concern and is known as "ditch waste". Ditch 4 carries wastewater from the floor drains and the cloudy chest in the paper mill.

With a color value of 10,000 to 25,000 CU the caustic extraction stage effluent contributes about ninety percent of the color load from the bleaching operation of a typical Kraft mill. The bleach plant effluent usually accounts for eighty to ninety percent of the total color load (7, 30, 60, 87). This emphasizes the importance of the ditch waste. The components of the ditch waste are about fifteen percent caustic extract and about eighty-five percent chlorine waste. A wastewater called "artificial ditch waste" was made by blending fifteen parts of caustic extract with eighty-five parts of chlorine waste. This eliminated wastes from other parts of the mill and yielded a wastewater which was more consistent in composition than the actual ditch waste. Artificial ditch waste was used for this research.

a. Massive Lime Precipitation The artificial ditch waste, as it was received in the laboratory, had a color of about 3,000 CU. The waste was precipitated with enough lime so that, upon recarbonation to

pH 7.6, the water had 300 CU. This 300 CU water was the raw wastewater used for this research.

#### 4. Gel Permeation Chromatography

Both the rate and capacity of adsorption are dependent, among other things, on the molecular weight or size of the adsorbate (53, 107). The second phase of this research was aimed at characterizing the raw wastewater and the wastewater treated with various sorbents with respect to molecular size. The technique used was gel permeation chromatography.

In gel permeation chromatography, a sample is applied to a porous gel, usually in a column. The pores in the gel are of such a size that molecules above a certain size cannot penetrate into the gel; they are therefore carried down through the column in the fluid passing around the gel beads and they emerge quickly. Other molecules may enter the pores. These molecules diffuse down through the column, through the pores, but at a slower rate than the larger molecules. The molecules are thus separated on the basis of size (23, 78).

The purpose of the gel permeation chromatography (GPC) was to determine if certain sorbents are specific for certain sized sorbates. If this is true, then perhaps sorbents can be used in combinations to produce a treated water which no sorbent could produce by itself.

In summary, the research described in this thesis was an attempt to replace activated carbon in the massive lime precipitation flow sheet with a sorbent which improved either the efficiency of the



the economics of the color removal process. Gel permeation chromatography was used in an attempt to characterize the effectiveness of the sorbents with respect to molecular size.

## CHAPTER II

### LITERATURE SURVEY

#### A. COLOR

##### 1. Definition of Color

Color is a human visual response to light reflected from or transmitted through a body. Three aspects of color are hue, brightness and saturation (102).

Hue refers to the name of the color and is dependent upon the dominant wavelength or the combination of wavelengths of light perceived. Most colored natural waters and wastewaters strongly absorb the blue wavelengths (350 to 480 mu) of incident white light. The remaining primary colors, red and green, add and are perceived as yellow (102).

Brightness is a measure of the light intensity or energy (102).

Saturation refers to the purity of the color, that is, how much white light is mixed with the colored light. The smaller the amount of white light mixed with a color, the greater is the degree of saturation (102).

The term "true color", which is synonymous with color in water and wastewater testing, means color caused by substances in solution in the water. "Apparent color" is caused by suspended matter as well (76).

Two common methods for measuring color are visual comparison methods and spectrophotometric methods. With the visual comparison

methods, an observer compares the color of a sample with the color of an arbitrary standard or with a glass disc which has been calibrated with an arbitrary standard. A spectrophotometer electronically measures the intensity of transmitted monochromatic light. This transmission may then be compared to the transmission through the standard (76).

The color standard used for this work is the widely accepted platinum-cobalt standard. The unit of color is that produced by 1.0 mg/l of platinum in the form of chloroplatinate ion (85).

Lambert's Law states that each layer of equal thickness of a medium absorbs an equal fraction of the light which travels through it; that is, monochromatic light intensity decreases exponentially as the length of the medium increases. Beer's Law states that the intensity of monochromatic light decreases exponentially as the concentration of the absorbing medium increases. These two laws are combined as the Lambert-Beer Law, which may be expressed mathematically as (76):

$$T = \frac{I}{I_0} = 10^{-kcl}$$

$$\text{or } A = \log \frac{I_0}{I} = kcl$$

where T = transmission

A = absorbance

k = extinction coefficient, a constant for a particular solution

c = concentration of the solution

$l$  = length of the absorbing medium

If, for a particular solution, plots of absorbance versus concentration for constant path length and absorbance versus path length for constant concentration yield straight lines, then the solution obeys the Lambert-Beer Law.

## 2. Causes of Color in Kraft Bleach Wastewater

Almost every pulp component or Kraft bleach reaction product has been accused of being the cause of color in Kraft bleach wastewater (38). Most often blamed are lignins and lignin degradation products (7, 14, 28, 38, 40, 58, 60, 68, 70, 84). Other suspects have been tannins (7, 106), carbohydrates (21, 38, 58), and other dissolved extractives (38, 58).

Hartler and Norrström (38) showed in Kraft pulps from spruce, ninety percent of the color is due to lignin, ten percent to carbohydrates, and less than one percent to dissolved extractives.

Christman and Ghassemi (16) isolated seven compounds which are degradation products of color in natural waters. These are vanillin, vanillic acid, syringic acid, catechol, resorcinol, protocatechuic acid and 3,5-dihydroxybenzoic acid. All of these aromatic compounds may be derived from lignin.

Pew and Connors (68) suggested phenyl substituted benzoquinone and coniferaldehyde groups are major contributors to the color of wood lignin.

Falkehag, et al (28), suggested Kraft lignin is the likely coloring matter in Kraft pulp and color is caused primarily by CH=CH double bonds conjugated with the aromatic ring and by quinone-methides and quinones. Minor contributions to color may be caused by chalcone structures, free radicals, and metal complexes with catechol structures.

### 3. Lignin--Definition and Structure

Wood is a heterogeneous material made up of three major components: cellulose, the hemicelluloses, and lignin (77). Lignin, which accounts for twenty to thirty-five percent of wood (71), has been the subject of intensive investigation by organic chemists for over a century, yet its structure and reactions have still not been completely elucidated. Originally defined as a compound, lignin is now considered to be a collective term for a whole series of similar, very large, structurally related molecules, perhaps analogous to other natural polymeric classes of compounds such as cellulose, starch, or protein (77).

Freudenberg (29) has summarized the concept of lignin on the basis of morphology: "Lignin is a substance which permeates the membranous polysaccharides and the spaces between the cells, thereby strengthening them. Its presence brings about physiological death of the tissue. It is a functional component of wood, and it occurs in mature wood as a preformed, completed substance."

The monomeric unit of lignin is considered to be the phenylpropane unit (66, 71, 75, 77), shown in Figure 1. Also shown in Figure 1 are the structures of coniferyl alcohol and guaiacyl propane, thought to be the precursors of lignin (16, 66, 75, 77).

In the lignin macromolecule, the monomeric phenylpropane units may be linked in a variety of ways both by ether and by carbon-to-carbon linkages (66, 75, 77). Carbon-to-carbon linkages may be phenyl-phenyl, phenyl-propyl, or propyl-propyl, and are highly resistant to chemical degradation. Multiple points of attachment may involve both ether and carbon-to-carbon linkages.

#### 4. Kraft Reactions

Though the Kraft process has been used commercially since before 1900, its reactions are poorly understood.

Heating lignin with alkalai solutions is thought to cause the splitting of certain phenyl-propyl ether linkages as well as propyl-propyl carbon-to-carbon linkages (66, 75). These reactions are common to the soda and Kraft processes.

In the Kraft process, sodium sulfate is added to make up losses of alkalai in the soda process. Sodium sulfate is reduced to sodium sulfide in the recovery furnace. The resulting solution contains both sodium hydroxide and sodium sulfide as active alkalais (66). It is thought that nucleophilic attacks by sulfide, hydrosulfide, and methyl mercaptide ions cause cleavage of ether bonds in the lignin polymer (26). The reaction products have not been completely elucidated.

































































































































