

Influence of the Chemical Properties of Wood on the Odor Produced by the Kraft Pulping Process

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Abstract—Chemical reactions occur between inorganic compounds and wood chips during the cooking step of the Kraft process. White liquor, which in this process is composed of sodium hydroxide (NaOH) and sodium sulfide (Na₂S), is mixed with wood chips in the digester in order to dissolve the lignin and produce wood pulp. However, other compounds are formed during the course of the chemical reactions. These compounds are volatile and malodorous due to the combination of the sulfur in white liquor and the carbon chains in lignin. This combination creates total reduced sulfur (TRS) compounds, which are malodorous gases responsible for the distinctive odor of the Kraft pulping process. This paper discusses the chemical composition of the wood species that contribute to these gas emissions. Gases are also released in other stages of the process, e.g., from the woodchips stored in the woodyard for factories that use only long pine fiber, from the digester, pulp washing filters, and from white, black and green liquor storage tanks. One way to reduce TRS emissions is through continuous attention to and correction of the pH levels of liquors containing sulfide ions.

Keywords— Kraft, Lignin, Mercaptans, Methoxy, Sulfur.

I. INTRODUCTION

This paper describes a literary review aimed at gaining a better understanding about the influence of the chemical components of wood, especially lignin, on the Kraft pulping process, and particularly on the odor produced by pulp and paper mills and clearly noticeable in their proximities.

Wood is composed of several chemical components such as cellulose, extractives, inorganic compounds and lignin, which is distributed unevenly according to the anatomical structure of the tree. The word lignin comes from the Latin term *lignum*, which means wood. Lignin is directly responsible for odor pollution due to methoxy, a functional group originating from the formation of thiols. Lignin is responsible for the high methoxy content in wood, corresponding to about 16% in softwoods and 22% in hardwoods (FAVARO, 2015).

The main environmental problem caused by pulp mills is odor, and a characteristic of the Kraft process are pollutant emissions that include both malodorous gases and particulate matter. The main contributors to the typical odors produced by pulp mills are total reduced sulfur (TRS) gases, which consist of hydrogen sulfide (H₂S), methyl sulfide mercaptan (CH₃SH), dimethyl sulfide mercaptan (CH₃)₂S and dimethyl disulfide mercaptan (CH₃)₂S₂, as well as sulfur oxide (SO_x) and nitrogen oxide (NO_x). Particulates consist mostly of sulfate, sodium carbonate and calcium (JERONIMO, 2000).

Some components are formed through reactions with lignin, such as the mercaptans methyl sulfide and dimethyl sulfide. The latter is produced through the oxidation of lignin-derived mercaptan groups, and the main emission sources of these gases are digesters, blow tanks and evaporators (RECH, 2007; CORREIA, 2008).

II. KRAFT PULPING PROCESS

The Kraft pulping process started in 1870 and 1871, when two U.S. patents were granted to A. Eaton for the delignification of wood with a mixture of sodium hydroxide and sodium sulfide (KLEPPE, 1970; CORREIA, 2008). However, the first industrial application of the Kraft process was only possible thanks to an important discovery by Carl F. Dahl in 1879, who discovered that the chemical waste resulting from the recovery of the chemical cooking in the soda pulping process could be offset by adding sodium sulfate to the boiler. The sulfate was then reduced to sulfite during the soda reduction phase of the recovery system. The sulfite was then recovered from the alkaline pulping liquor (KLEPPE, 1970; KLOCK et al., 2013).

The process involves the high-temperature high-pressure chemical digestion of wood chips in white liquor, which is an aqueous solution of sodium sulfide and sodium hydroxide. The solution chemically dissolves the lignin, which holds the cellulose fibers together (JUNIOR et al., 2008; KLOCK et al., 2013). According to Kleppe (1970), the main reasons for the success of the Kraft process are as follows:

- An efficient and economical chemical recovery process for pulping materials;
- All commercial timber species can be used in this process;
- The discovery of chlorine dioxide as a pulp bleaching agent, its efficient use in the Kraft pulping process, and inexpensive pulping methods;
- Kraft pulping produces high strength cardboard paper whose properties are superior to those manufactured by other processes.

A negative aspect of the Kraft process is the characteristic odor it produces, caused by the emission of reduced sulfur compounds generated by the delignification of wood in general (RECH, 2007; MARTINS, 2011). The most common of these compounds are hydrogen sulfide, methyl sulfide mercaptan and dimethyl sulfide mercaptan. Methyl sulfide and dimethyl sulfide mercaptan are formed in reactions with lignin. Dimethyl sulfide mercaptan gas is formed via the oxidation of lignin-derived mercaptan groups. These compounds are emitted from several points in a pulp mill, but the main sources of these gases are digesters and blow tanks, as well as direct contact evaporators (RECH, 2007; CORREIA, 2008).

2.1 Chemical Composition of Wood

According to Cardoso (2009), wood has a complex chemical structure. Its vegetable tissues are composed of several chemical constituents distributed unevenly throughout the anatomical structure, varying within the same species and even within the fibrous wall. The chemical constituents of wood consist of mineral matter, secondary constituents, cellulose, hemicellulose and lignin. Table 1 describes the composition of these materials according to species.

Table 1: Biomass composition

Biomass	Cellulose	Hemicellulose	Lignin	Extractives
Softwoods	45±2%	30±5%	20±4%	5±3%
Hardwoods	42±2%	27±2%	28±3%	3±2%
Grasses	37±2%	29±2%	19±2%	15±2%

2.2 Lignin: A Component of Wood

Lignin is one of the main constituents of wood, corresponding to an average of 15 to 35% of plant tissue. Its structure varies according to the nature of the wood group (Angiosperms or Gymnosperms), the plant's age (early or late wood), and the tree's growth conditions (normal wood or reaction wood) (CARDOSO, 2009).

Lignin strengthens the cell walls and helps transport water, and together with extractives, prevents degradation by protecting the tree against pathogens, insects and herbivores (HATFIELD & VERMERRIS, 2001; BRUYAN, 2009; FINGER 2015).

Lignin is a homogeneous, branched, amorphous and polyphenolic material that derives from the enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. These alcohols, also known as monolignols, have differences in the substituent groups of the aromatic ring and are the precursors of the units known as p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), respectively (LIN, 1992; SALIBA, 2001; BOERJAN et al., 2003).

According to Lin (1992) and Saliba (2001), the chemical structures of the precursors of lignin units behave as illustrated in Fig. 1.

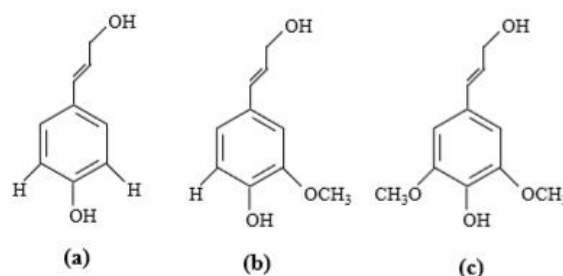


Fig. 1: chemical structure of the precursors of lignin units: (a) p-coumaryl alcohol, (b) coniferyl alcohol (c) sinapyl alcohol.

The dehydrogenative polymerization of monolignols causes them to bind to one another through C-C and R-O-R' bonds, forming a heterogeneous structure, as depicted in Figure 2 (PEREZ et al., 2002).

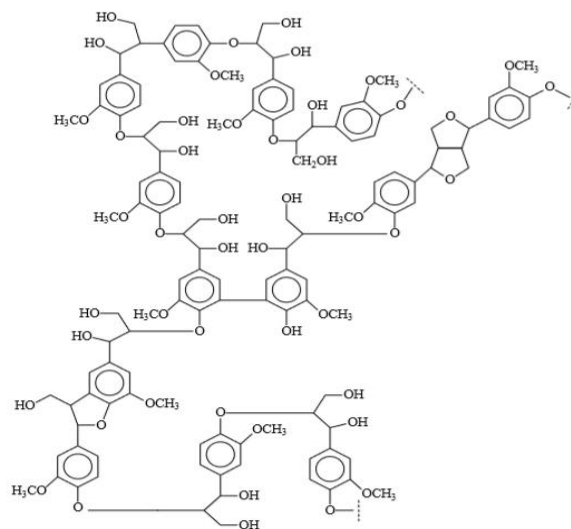


Fig. 2: part of a chemical structure of lignin.

The bonds between phenylpropane units and functional groups give lignin a unique and complex structure. The lignin macromolecule also contains a variety of functional groups that affect its reactivity (FAVARO, 2015).

The main functional groups of lignins are (ARGYROPOULOS et al., 2002; FROASS et al., 1996; KUKKOLA et al., 2004; SENAI, 2013; FAVARO, 2015):

- Methoxy groups (-O-CH₃): the most characteristic functional group of lignin (92 to 96 units per 100 phenylpropane units [PPU]). Although hemicelluloses contain some methoxy groups, their content in wood comes almost entirely from lignin, corresponding to about 16% in softwoods and 22% in hardwoods. Hemicelluloses are responsible for the characteristic odor of Kraft pulping, originating from the formation of mercaptans.

- Hydroxyl groups (-OH): these groups may be phenolic or aliphatic. Only a small portion of them is free, since most of them bind to neighboring phenylpropane units.
- Free phenolic hydroxyl groups, corresponding to 15 to 30/100 PPU.
- Carbonyl (-C=O) and carboxyl (-COOH) groups, corresponding to 10 to 15/ 100 PPU.
- Ether groups (R-O-R'): may be aromatic or aliphatic.
- Double bonds (-C=C-).
- Ester groups (R-COO-R').

The main groups are illustrated in Fig. 3, which shows the lignin structure proposed by Casey in 1980.

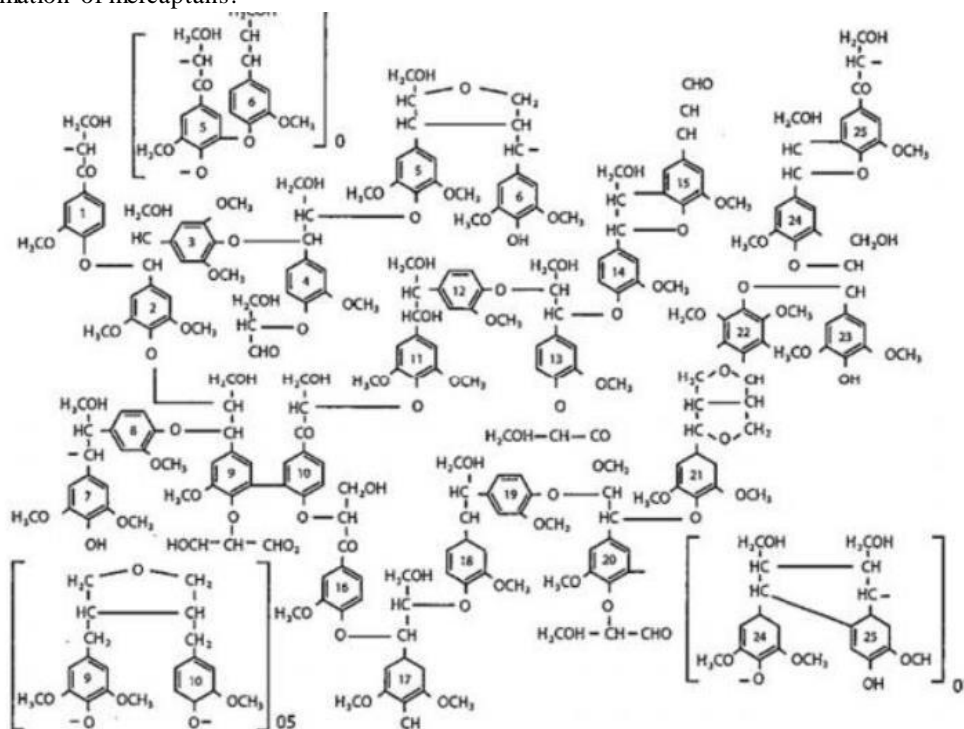


Fig 3: proposed structure of lignin.

2.3 Methoxy Groups

Lignin-rich woods and xylans tend to contain larger numbers of methoxy groups. Methoxys are present in greater number in hardwoods. They appear in the monomeric groups guaiacyl and syringyl, mostly in glucuronic acid, which is the xylan of hardwoods, and in hexuronic acids formed in Kraft digestion. Methoxys are precursors of the formation of mercaptan because they react with sulfur to form the methyl sulfide mercaptan compound (FOELKEL, 2013).

Lignins are formed from the three basic precursors mentioned earlier herein. The p-coumaryl compound does not contain methoxy, while coniferyl and synapyl

have 1 and 2 groups per mole, respectively. The methoxy group is considered a functional group characteristic of lignins and their derivatives, and it is extremely important to determine its content for the analysis of the macromolecule (MORAIS et al., 1992). Figure 4 illustrates the chemical structure of sinapyl alcohol (LIN, 1992; SALIBA, 2001).

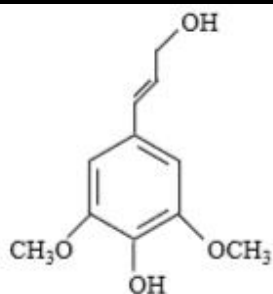


Fig. 4: chemical structure of sinapyl alcohol.

2.4 Formation of Mercaptans

According to Foelkel (2013), methyl sulfide mercaptan is formed through reactions between the methoxy groups from hardwood lignin and xylans. The reaction between these methoxys and the hydrosulfide ion (HS^-) occurs when the ion begins to form as the pH level of the liquor decreases through the consumption of caustic soda by wood. Methyl sulfide mercaptan is the first mercaptan to be formed, when the pH level is still high. By becoming available in this environment, it can be converted into dimethyl sulfide mercaptan as the pH decreases and the number of hydrosulfide ions increases. Reactions between hydrosulfide ions and methyl sulfide mercaptan lead to the formation of dimethyl sulfide mercaptan, after which dimethyl disulfide mercaptan is formed through further reactions with the hydrosulfide.

According to Silva et al. (2001), due to their pronounced nucleophilicity, hydrosulfide ions divide the methoxy groups of lignin to form methyl sulfide mercaptan. This mercaptan is formed during Kraft cooking and is dissolved in black liquor in low concentrations. It is a weak acid that dissolves in aqueous media. It is also extremely fetid, even at low concentrations (RECH, 2007). Due to its highly unpleasant odor, which most humans can detect even at low concentrations (odor detectable starting at 0.0016 ppm), methanethiol is used to add odor to several hazardous odorless gases (MITCHELL, 2002). The main components of the Kraft odor are four gases: hydrosulfuric gas, methyl sulfide mercaptan, dimethyl sulfide mercaptan and dimethyl disulfide mercaptan. These are compounds of low molecular weight and low solubility in hot water, which spread easily through the atmosphere. These compounds are all measured together, but they can also be measured individually to determine their individual concentrations, and they form the set of reduced sulfur compounds (FOELKEL, 2013).

According to the Agency for Toxic Substances and Disease Registry (ATSDR, 1992) and Mitchell (2002), inhaling methyl sulfide mercaptan can lead to neurological disorders and death. However, the ATSDR provides no information about limits of concentration and

their consequences to health. Figure 5 illustrates the behavior of the molecule, according to Sixta et al. (2006).

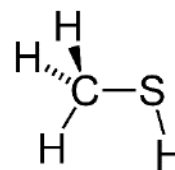


Fig. 5: methyl sulfide mercaptan molecule.

2.5 Pollutant Emissions

The sulfur compounds responsible for the odor characteristic of the Kraft process are formed in the reaction between hydrosulfide ions and the methoxy groups of lignin. Due to their strongly nucleophilic nature, hydrosulfide ions divide the methoxy groups to form methyl sulfide mercaptan and the corresponding catechol structure (Figure 4). Methanethiolate ions may separate the methoxy group to form dimethyl sulfide mercaptan or they may become oxidized, forming dimethyl disulfide mercaptan. The weakest nucleophiles are hydroxyl ions, whose reaction with the methoxy groups is negligible (GIERER, 1985; DA SILVA, 2001). Fig. 6 demonstrates, according to Gierer (1985), how divisions occur in a process also known as cleavage.

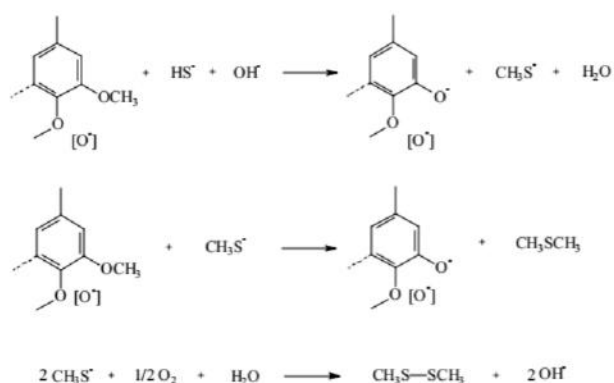


Fig. 6: division of methoxy groups of lignin, hydrosulfide ions and methanethiolate.

2.6 Ways to Prevent or Reduce the Production of Odor

The odor produced by Kraft pulp and paper mills is strongly influenced by two factors. Firstly, odors are not emitted from a single source but are generated at various locations in the manufacturing plant, and a change in the process may reduce the emissions from some of these sources but may also directly impact others. Secondly, the limits established for the odor emanating from hydrogen sulfide and methyl sulfide mercaptan are in the order of parts per billion (ppb), making it difficult to keep the ambient air concentrations consistently below these values in the proximities of these mills (RECH, 2007).

Foelkel (2013) states that, at low concentrations, the odor is not harmful to people's health, but it can become a source of discomfort or an offensive stench to those who live in the surroundings of pulp and paper mills. One way to reduce the generation of these gases is to use anthraquinone under optimized conditions of delignification. The use of anthraquinone increases the yield of pulp and improves its quality, in addition to reducing the emission of TRS (CARASCHI et al., 2005). TRS emissions can also be reduced through continuous attention to and correction of the pH levels of liquors containing sulfide ions. The pH level can be adjusted inside the digester, in the evaporation and at the entrance of the digester in the recovery boiler (FOELKEL, 2013).

2.7 Use of Anthraquinone in the Kraft Process

Anthraquinones are a class of compounds applied in the production of typical products via different manufacturing processes. These compounds are widely used in the industry, even in the field of cosmetics. Toxic contaminants may be present in some anthraquinone manufacturing processes, which may thus limit their approval by inspection agencies. Therefore, not anthraquinone, but the presence of contaminants is banned (FOELKEL, 2013).

According to Gomide and Oliveira (1979), Kraft pulping processes that use anthraquinone give rise to wood polysaccharide oxidation reactions and hydrolysis of the lignin ether bonds. This leads to oxidation of the reducing group of carbohydrates, stabilizing them against terminal depolymerization reactions, which in turn increases the yield because this stabilization protects the carbohydrates against degradation and solubilization reactions.

The research findings of Jerônimo et al. (2000) indicated that the use of anthraquinone improved delignification, thereby reducing sulfidity. According to their findings, soda-anthraquinone delignification yields slightly lower results, but offers a promising potential for manufacturing plants that generate odors which pose a serious problem. Silva et al. (2002) used anthraquinone in the eucalyptus kraft pulping process, and evaluated the impact caused by its use based on their results. According to these authors, the use of anthraquinone decreased the formation of TRS, reducing the formation of methyl sulfide mercaptan by up to 63%, and also retaining a larger content of xylans. Starting at the beginning of this century, the most modern plants have been operating with much more high-tech digesters, as well as odor-free recovery boilers. As a result, the effects of anthraquinone have not been as significant as in plants that use older technology digesters operating above their design capacities and producing pronounced odors (which is no longer the case in state-of-

the-art digesters and recovery boilers). This new situation has led several older mills to still use anthraquinone as a pulping aid (with or without other reagents) (FOELKEL, 2013).

III. CONCLUSION

As can be seen, the chemical components of wood are directly linked to the unpleasant odors generated in the Kraft process. These odors are produced by lignin, which not only interferes in the quality of the final product but also impacts the quality of the air around pulp mills, allied to the sulfur that is inserted into the process through sodium sulfide. This study emphasizes the importance of understanding the reactions that involve lignin constituents, such as the cleavage process of methoxy groups that leads to the formation of methyl sulfide mercaptan, one of the malodorous components of TRS. The offensive smell produced by the process is a particularity of each plant, as pointed out in this paper. The chemical components may vary in quantity from one tree to another, just as factories may operate with equipment using technologies that are more advanced than others, which in this case helps to minimize the odor, and also the daily operating conditions in general. Although several studies have focused on reducing the emission of these TRS gases using anthraquinone (AQ), and despite the claim by some authors that AQ is not a product harmful to human health, it is impossible to conclude that the product of the reaction between AQ and lignin is innocuous. Given the fact that the lignin structure is extremely complex and still largely unknown, several studies in this field are still being conducted.

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