

**INFLUENCE OF EXTRACTIVES ON THE BLEACHABILITY
OF BATCH EXTENDED DELIGNIFIED KRAFT PULPS**

by

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DEDICATION

**I would like to dedicate this dissertation to
my parents Yuhua Dai and Jialan Chen and my wife Wei Wei.
Without their anticipation, understanding,
support and encouragement,
I would not be where I am.**

BIOGRAPGY

Qizhou Dai was born in August 1970 in Henan, a central province of China. He grew up in Wuhan, the largest central city in China. He finished his primary and secondary education in Wuhan. After graduating from high school in 1988, he went the University of Science and Technology of China, one of the top universities in China. He received his B.S. degree in Polymer Physics in the Department of Material Science and Engineering in 1993.

In fall 1993, he went to Guangzhou Institute of Chemistry, Chinese Academy of Sciences, a research institute located in southern China, for his graduate education. In the process, he heard about the Wood and Paper Science program in North Carolina State University for the first time. Dr. Hou-min Chang, Dr. Josef Gratzl and Dr. Chen-Loung Chen in Wood and Paper Science, NCSU were the guest professors in that institute. After receiving his M.S. degree in Polymer Science in 1996, he stayed in the institute as a researching staff for half a year. In Spring 1997, he came to US and started working towards his Ph.D. degree in the Department of Wood and Paper Science, NCSU.

The author was married in November 1996 to Wei Wei and their first child was born in October 2001.

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CHAPTER I

INTRODUCTION

Wood is one of the most abundant natural composite materials. The main components of woods are cellulose, hemicellulose, lignin and extractives. These compositions change with different wood species, wood age, locations and wood morphology. The typical compositions of softwood and hardwood are:

Table 1-1. The Main Components of Natural Wood

Wood Species	Cellulose	Hemicellulose	Lignin	Extractives
Softwood	42±2%	27±2%	28±3%	3±2%
Hardwood	45±2%	30±2%	20±3%	5±3%

The advantages of wood as the renewable fiber source include year-round availability, relative stability during storing, the ability to serve as a waste resource from other wood product operations, low content of inorganic contaminants and low cost of growing. Currently, more than 94% of pulp fiber is from wood globally and in countries such as the United States, the amount is as high as 98%.

The main purpose of pulping is to separate the fibers in the wood. The wood fibers can be separated either by mechanical methods or by chemical methods. Chemical pulping is a process in which lignin is almost completely removed so that wood fibers can be separated. Kraft pulping is the dominant chemical pulping method, which is performed with a solution of sodium hydroxide and sodium sulfide. About 70% of the chemical pulp used today comes from the kraft pulping process. The conventional kraft pulps with a kappa number of 30-35 for softwoods and 18-20 for hardwoods can be achieved by removing about 90-95% of the natural lignin in the wood. The removal of the

highly condensed residual lignin only by extending the conventional kraft pulping usually leads to the loss of yield and a poor pulp strength, which is due to the degradation of carbohydrates. The bleaching process is used to prevent the yield and strength loss by selectively removing the residual lignin without hurting carbohydrates under milder conditions than those used in the pulping. The bleaching process is a multistage oxidation and caustic extraction sequence in which chlorine and/or chlorine dioxide is commonly used. The amount of chlorinated organic compounds formed in the bleaching effluent is based on the amount of chlorine consumed by the pulp. Some chlorinated organic compounds can be toxic and carcinogenic.

In the pulping process, almost all the inorganic and organic wastes are recovered. The main pollution in the pulping and paper industry comes from the chlorinated organic compounds in the bleaching effluent. Due to increasing environmental pressure, it is necessary for the pulp and paper industry to develop new methods to reduce the amount of organochlorine compounds in the effluent coming out of bleaching plants. As a result, many new technologies aimed at lowering the lignin content or enhancing the bleachability of the pulp entering the bleach plant without sacrificing the quality of the kraft pulp have been developed. By modifying the pulping process, such as adding additives to the conventional kraft pulping process and extending the delignification process, the lignin content of pulps has been reduced. A lower kappa number of the unbleached pulps results in a decrease in the usage of chemicals in bleaching and a decrease in the amount of AOX discharged from the bleaching plant.

Extended delignification is a new technology, which lowers the kappa number of the kraft pulp without hurting the pulp strength by selectively removing additional amounts of lignin during the pulping process. Four basic principles of the extended delignification have been proposed [1]:

- (1) Level out the alkali concentration (keep it lower at the beginning of the kraft pulping, and higher toward the end, than in the conventional process).

- (2) Keep the HS^- concentration high, especially at the start of the bulk delignification.
- (3) Keep the dissolved lignin and Na^+ concentration low, especially toward the end of cooking.
- (4) Keep the temperature low, especially at the beginning and end of pulping.

Currently several systems for extended delignification have been developed and some of them have been marketed. These well-known extended delignification processes, including Modified Continuous Cooking (MCC) [2], Extended Modified Continuous Cooking (EMCC) [3], Isothermal Cooking (ITC)[4], SuperBatch [5], Lo-Solids [6], EnerBatch [7] and Rapid Displacement Heating (RDH)[8], have been thoroughly studied and have been applied in the industry.

Besides the kappa number, other factors, including the wood species, the nature of the residual lignin in kraft pulps, affect the bleachability of kraft pulps. The extractives are the minor components of woods and play a comparatively minor role in determining the pulp bleachability, compared to factors such as wood species and residual lignin structures. "Extractives" is used as a collective name for the nonstructural wood constituents, which are organic compounds that can be extracted by organic solvents. Sometimes the term "resin" is used instead of extractives. Resin refers to those organic substances in wood and pulp that are soluble in neutral organic solvents and insoluble in water [9]. Usually, the extractives in pulps affect the bleachability of pulps negatively, such as causing a lower brightness and a higher brightness reversion of the kraft pulp [10] or consuming more bleaching chemicals [11]. Experiments have shown that the bleachability of pulps after an organic solvent extraction [12, 13] or prepared from the organic solvent extracted chips [13] was much higher than that of the pulps before the extraction. Pulps produced from wood species with a high extractive content have a lower bleachability than that from wood species with a lower extractive content [14, 15]. Efforts to lower the extractive content of pulps,

such as improving the debarking efficiency [16], presteaming [17] and seasoning [18], also result in enhancing the bleachability of pulps.

LITERATURE REVIEW

Role of Extractives in Kraft Pulping and Bleaching

The term “extractives” is used to refer to the nonstructural components of wood and bark. Most extractives are organic substances soluble in organic solvents, including polyphenols, terpenoids, fats, waxes, organic acids, complex polysaccharides and nitrogenous compounds [19]. Some of them are unsaponifiable (hydrocarbons, sterols, various alcohols, aldehydes, etc), and some are saponifiable (fats, sterol esters). The amount of extractives and their composition vary with respect to the botanical families, wood species, growth regions and tissues. The amount of extractives and their components also vary according to the solvent used for the extraction.

The amounts of extractives vary widely between families and species. The wood species is probably the most important factor that affects the extractive content and extractive components of the wood. Usually a higher extractive content is found in hardwoods than in softwoods. Southern and tropical wood species have higher extractive content than northern wood species. In general, more acidic compounds, such as acetic acid, are found in the hardwood. The softwood has a high concentration of resin acids.

Within the same wood species, more extractives can be found in trees grown in a harsh environment because some of the extractives such as fatty acid serve as the food deposit. Therefore, it is not surprising to find more extractives in compressed wood than in regular wood [20]. Old wood contains more extractives than young trees [21, 22, 23]. Trees harvested in the winter have a higher extractive content than that in the summer [24, 25]. Contradictory observations exist concerning the effect of the growth rate on the amount of

extractives formed [19]. Rapid growth wood appears to result in increased heartwood extractives in eucalyptus [26]. The total extractive content in trembling aspen decreases in the fast growing trees [27]. The total heartwood extractives in northern red oak and black walnut failed to show any relationship with the growth rate [28]. The extractive composition also varies with the different wood species. Hardwoods have a high content of unsaponifiable compounds than softwoods. More resin acids can be found in the softwood than in the hardwood.

The distribution of extractives varies even in different tissues within the same tree. More extractives are found in the bark than in the wood [29, 30]. The heartwood contains more extractives than the sapwood [27, 31, 32]. From the base to the top of the tree, the content of extractives increased for birchwood [32]. However, for scotch pine, the yield of extractives from the heartwood decreases with an increasing trunk height [33]. For the loblolly pine, the latewood contained less extractive than the earlywood [34]. However, the latewood in the heartwood had more extractives than the earlywood in the same annual growth ring for *Pinus radiata* [35]. For larch, fibers from the latewood contained a larger amount of water-soluble and ether-soluble extractives than the earlywood [36]. Almost all thin-walled parenchyma cells contain extractives, and they may be completely filled in some heartwoods. The thin-walled vessels in heartwood may also contain extractives if the heartwood contains a large amount of extractives. The fiber may contain extractives in their lumen in some species with a very large extractive content [37]. Different extractive compounds occupy different morphological regions in the wood. The resin acids are mainly in the resin canals. The fats and waxes are located in the ray parenchyma. More polyphenolic compounds are found in the heartwood so that the heartwood has a darker color than the sapwood [38]. Free resins and fatty acids are present in only trace amounts in the sapwood of pines, but are quite abundant in the heartwood [39]. Neutral lipids are dominant in the sapwood [32].

The wood extractive content is greatly affected by the seasoning, or storage. Throughout the seasonal storage, due to the respiration, emission,

auto-oxidation, fungal attack and other factors, the wood extractives decline rapidly during seasoning [40, 41, 42, 43]. The total acetone extracts were decreased by over 56% after three-month seasoning for *Eucalyptus globulus* healthy wood [44]. With the attack of extractive-degrading fungi, the extractives were decreased by up to 75% [45]. The extractive loss during storage was estimated at 1.2% per month for *Eucalyptus globulus* chips [46]. For *Pinus sylvestris*, the decrease in extractives content during the storage was 4% per month for the logs and 8% per month for the chips [47]. After seasoning, the ratio of unsaponifiables to saponifiables increased because of the bio-hydrolysis of steryl esters, glycerides and waxes [44, 48]. For the decayed wood, the microorganisms convert many of the neutral resins, including unsaponifiables resin, into low molecular weight saponifiable resins [31]. The carbohydrates are also attacked by the fungus. Usually, during the storage, the total extractive content decreases and then increases, probably owing to the degradation of the carbohydrate fraction in woods [43]. In addition, these conditions can result in abnormal discoloration of polyphenols [49]. The oxidation products of them are much darker than the original substances. However, such discoloration may not affect the bleachability of the pulp prepared from the discolored wood.

Kraft pulps are cooked under alkaline conditions. There are some extractives, such as terpenes, that are inert to the pulping conditions. However, most extractives, especially the acidic and polyphenolic compounds, react easily with the pulping chemicals. Naturally, during pulping almost all the saponifiable compounds, such as fatty acids and polyphenols, are completely saponified and converted to their sodium salts under alkaline conditions [50]. Therefore, most of the saponifiables can be removed during the pulping process. Almost all the unsaponifiable compounds are non-polar, uncharged, hydrophobic compounds. They are insoluble in water and most of them can survive the pulping process and finally stay in the pulp. It's well known that the unsaponifiables content of pulp is higher than that of the original wood, almost twice as much as in the wood [51], which indicates that almost all unsaponifiable compounds survive the

pulping process and stay with the pulp. The softwood contains only a small amount of unsaponifiables. The extractive content in the softwood kraft pulp is as low as 0.2% - 0.5%, which is comprised largely of unsaponifiables. The extractive content remaining in hardwood pulps is about 0.5% - 1.0%, depending on the wood species and debarking efficiency [52]. Previous study has shown that these unsaponifiables are the most troublesome in the kraft pulping [51], and they may have a large influence on the bleachability of kraft pulps. Hardwood pulps have more bleaching problems than softwood pulps possibly due of their higher unsaponifiable compound content and lower kappa number.

Of all the extractives retained in the kraft pulps, steryl esters and sterols are the major portion of the total lipids in the hardwood. The content of steryl esters, waxes, sterols and fatty alcohols was higher for hardwood pulps (such as aspen) than softwood pulps. The kraft cooking caused no structural changes of this fraction [53]. Triglycerides were found to be always the most difficult type of extractives to remove [54]. Triglycerides, steryl esters and waxes in unbleached pulps are considered to be the major contributors to pitch problems and poor bleachability [55].

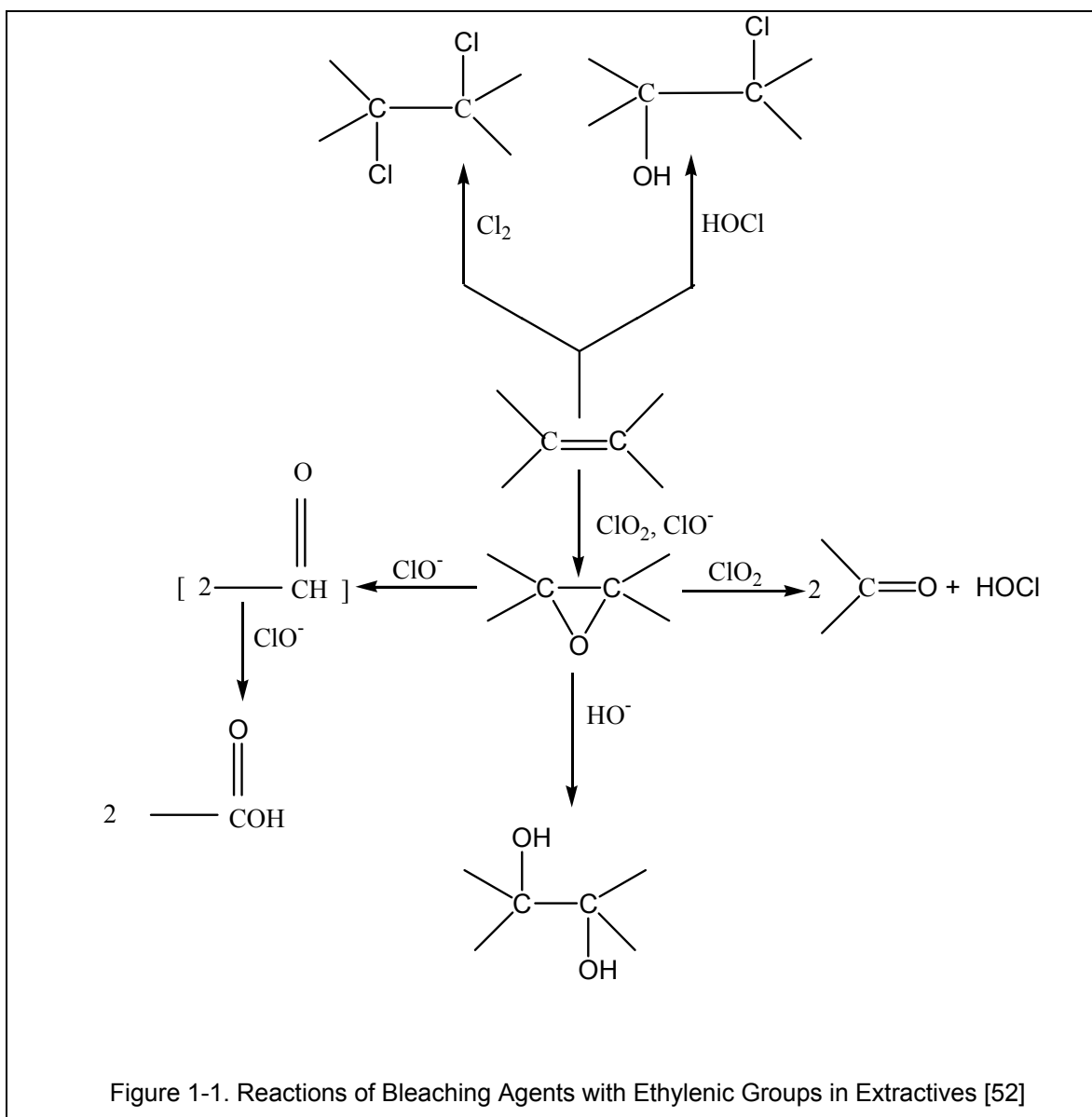
However, a considerable amount of unsaponifiables can be removed by kraft pulping. The dispersion of the unsaponifiables in the cooking liquor is due to the micellar solubilization by fatty acids and resin acids in the form of sodium soaps [56, 57]. These soaps serve as the surface active components to form micellar particles. The hydrophilic heads of the soap molecules turn outside towards the solution while the hydrophobic tails turn to the inside of the micelles. The unsaponifiable compounds are enclosed by the hydrophobic tails. These micelles make the unsaponifiables suspend stably in the alkaline cooking liquor. There is a critical concentration of the surface active agents, above which the micelles can be formed. This is called the critical micellar concentration (CMC). In the softwood kraft cooking, the CMC is usually exceeded and most of the soaps form micelles. In the kraft pulping of hardwoods, due to the high content of unsaponifiables and the low resin acid content, a large portion of these

unsaponifiables will stay with the wood chips and end in pulps. The non-polar substances can be dispersed further if some surface active chemicals are added to the cooking liquor [58, 59, 60]. Experimental results indicated that the resin content of hardwood pulps like aspen and birch, was lowered by 70% and 30% respectively by adding synthetic surfactants or tall oil [61].

Under the alkaline conditions, the fibers are negatively charged and the surface charge increases with the increase of pH. Therefore, when the chips are cooked at a high pH condition, the electrostatic force prevents the precipitation of micelles onto the fiber surface. At the end stage of the cooking, when the alkali concentration is low, the surface charge of fibers is also low. Some of the extractive formerly suspend stably in the cooking liquor may precipitate on the fiber and stay with the fiber. On the other hand, when the pH is low, the rate of the precipitation of the condensed lignin is accelerated [38]. Some of the lignin fragments form larger, more condensed lignin molecules due to the condensation reactions. These condensed lignin molecules are insoluble in the liquor and precipitate on the fiber surface. Studied by electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS), the fiber surface was found to be covered with a higher concentration of extractives and lignin than the average content through the fiber [62, 63, 64, 65]. The surface extractives can be largely removed by the organic extraction [66]. And, alkaline extraction of the pulps usually results in the increase of the surface lignin content.

The extractives that stay with the pulps will be carried over to the bleaching processes. Some of them are inert enough to be carried over to the paper-making process. There are several possible mechanisms by which the extractives affect the bleachability of the pulp. The first one is the reaction mechanism. Some of the extractives with unsaturated structures can react with bleaching chemicals such as Cl_2 , ClO_2 , etc [52]. The mechanism of the reactions of Cl_2 and ClO_2 with $\text{C}=\text{C}$ double bonds is shown in Figure 1 [52]. Some of the saturated structures in extractives might also be oxidized [67]. The phenol

compounds or lignin fragments, such as stilbene, can react easily with the bleaching chemicals [68]. Unsaturated fatty acids, resin acids, unsaturated sterols, aldehydes were found to be completely oxidized in the bleaching [15, 68, 69]. Part of the bleaching chemicals is consumed by these extractives, which lowers the bleaching efficiency of the bleaching agents.



Secondly, some extractives are inert to bleaching chemicals, such as extractives in the wood barks [16]. Only minor changes were found in the structure of free fatty acid and neutral lipophilic extractives during the bleaching. Steryl esters, triglycerides remain essentially unaffected [68, 69, 70]. Some of these extractives are hydrophobic and concentrate on the fiber surface. This part of extractives may block the penetration of the bleaching chemicals into the fiber wall or prevent the diffusion of lignin fragments out of the fiber wall. In addition to the extractives, the surface lignin, originated from wood fibers or formed during the cooking, is more condensed and less reactive to the bleaching chemicals [64]. They also may affect the bleachability by a blocking mechanism.

Some of the wood species have a high content of colored polyphenolic compounds, such as tannins and flavonoids. Some of these colored compounds can survive the bleaching process and lower the final brightness [14, 71, 72, 73], and some may form specks in the bleached pulps [73, 74]. This is noticeable in the eucalypts species [37] and *Pinus banksiana* [75]. The amount and the nature of these extractives have an adverse effect on the color of the pulp, greatly exceeding that of the lignin. Besides the natural extractives, some of the compounds generated during the cooking also have the coloring effect [75]. It was found that the time of contact of the pulp with the black liquor during the pulping was a factor influencing the bleachability of the pulp. The colored compounds were highly resistant to oxidation and were not easily removed either by washing with water or with alkali [76]. It was proposed that the natural compounds containing the gallic acid moiety were oxidized to quinones during the pulping. These compounds in the black liquor adhered strongly to cellulose in the pulps [77].

In the industry, multiple bleaching stages are used. Different stages have different extractive removal efficiencies. The changes in the extractive content depend on the nature of the bleaching chemical and its ability to penetrate the extractive or to interact with its surface [16, 70]. The alkaline extraction or caustic washing is the most practical way to prepare a high brightness pulp with a low

content of extractives [78]. The chlorine dioxide bleaching can remove 25-30% of the extractives in hardwood pulps [79]. Up to 60% of the extractives in the pulps were removed by the peroxide bleaching [80] though little hydrolysis of fatty acid esters occurred. The content of extractives on the surface of pulps was decreased considerably by oxygen treatment, less by peroxide, and only minimally by ozone or chlorine dioxide [63]. Ozone was found to remove significantly more of the surface lignin than the average decrease in the pulp lignin content. The fraction of surface lignin removed by HOOH and oxygen was smaller than the total decrease in the lignin content. The surface lignin removal efficiency of ClO_2 was strongly dependent on the number of treatments [63].

Many pretreatments are very effective to remove extractives in wood chips and pulps. Besides improving debarking efficiency, presteaming and seasoning as mentioned before, a large amount of tannin-like polyphenols in some tropical hardwood chips can be removed by hot water pretreatments. A decrease of the consumption of alkali in pulping, improved pulp color and reduced precipitation tendency of liquor were the results [14]. Polyphenolic compounds can also be largely removed by pretreatments with the residual alkali in black liquors before the pulping [71]. Pretreated with a hot sodium carbonate solution, most of the extractives in pine chips can be removed [81]. By heating the logs or wood chips at 90-160°C before the storage, the amount of extractives in woods is reduced [82] and the brightness of the wood pulp is increased [83]. With three weeks of fungal treatment, the wood resin in aspen could be removed by 14%. The triglycerides and fatty acids were significantly reduced. Unsaponifiable wood-resin components such as sterols, steryl esters and waxes, were partially removed [84]. With light beating of kraft pulp in a weak alkaline medium before the conventional bleaching, impurities in the pulp dissolved easily into the bleaching liquors. Less bleaching chemicals were consumed than in the conventional bleaching and pulps with a higher brightness and a lower color reversion were produced [85].

Extended Delignification

Extended delignification is the name given to the process of producing pulps at a low kappa number by modification of the kraft pulping system without severe pulp yield loss and pulp strength loss [86, 87]. The main driving force of the extended delignification relates to the environmental factors. When less lignin arrives at the bleaching plant, the potential environmental impact of the bleaching effluents is reduced. The second concern is the cost, since bleaching chemicals cost much more than pulping chemicals. Pulping is still the cheapest method to remove the lignin [2].

There are two types of extended delignification systems, batch systems and continuous systems. Each system has several commercial variants. There are two commercial systems for the batch extended delignification: GL&V RDH (Rapid Displacement Heating) system and Sunds Defibrator SuperBatch system. For the batch systems, the basic idea is the liquor displacement. At the end of the pulping, the black liquor is displaced into separate pressurized vessels for storage from where it can later be used to pre-treat chips, heat chips and white liquors. In general terms, the operating cycle of a batch delignification process is in the following order [3]:

- (1) The digester is filled with chips.
- (2) Warm black liquor at about 130°C is pump in from the bottom of the digester to a certain volume.
- (3) Hot black liquor at about 160°C is pumped in from the bottom upward to displace the warm black liquor.
- (4) Hot white liquor at about 165°C is pumped in to displace some of the hot black liquor.
- (5) The white liquor is heated up to the cooking temperature.
- (6) It takes a certain time at cooking temperature to finish the cook.
- (7) At the end of cooking, brown stock washer filtrate is pumped into the digester to displace the hot black liquor and to stop the reaction. The displaced liquor

goes first to the accumulator at highest temperature, and later to the intermediate or lower temperature ones.

(8) The pulp in the digester is blown out.

There are several advantages of the liquor displacement. With the liquor displacement, the heat value of the black liquor can be captured, which lowers the consumption of the high pressure steam. Due to the high initial temperature after the hot white liquor displacement, the liquor circulation time during cooking is reduced. The role of digester circulation changes from heat transfer to mass transfer. The bulk delignification is therefore greatly accelerated. The high sulfidity black liquor impregnation increases the selectivity during cooking. The higher liquor to wood ratio makes the liquor penetration more uniform, and lowers the rejects yield. Displacement of the pretreatment black liquor with the white cooking liquor reduces the dissolved organic solids in the digester. Studies have shown that by using the extended delignification systems, the kappa number of softwood kraft pulps can be below 20 and the kappa number of hardwood kraft pulps could can be below 10 without penalties in the pulp strength [2].

Extractive Problems in Extended Delignification Systems

For the batch extended delignification systems, during the various pretreatments and post treatments described above, the chips are treated with black liquors of different temperatures and alkali concentrations. The liquors were accumulated from different stages of the previous cook and reused [3, 86]. In these processes, due to the multistage black liquor pretreatments and recycling, there is greater opportunity for the extractives to accumulate in the black liquor and to precipitate on the fiber surface than in the conventional kraft pulping. This may make the extended delignified kraft pulps harder to bleach than the conventional kraft pulps. Previous work has shown that hardwood pulps cooked using the RDH process were harder to bleach when compared with the Kraft-O₂ pulps [88].

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CHAPTER II

RESEARCH OBJECTIVES

Many studies have been done on the optimization and modification of the cooking conditions to determine the effect of these changes on the extended delignification process and pulp properties [1, 2, 3, 4, 5, 6, 7, 8]. Most of these studies did not focus on how these changes of cooking conditions affect the extractive content of pulps, and how this will finally affect the bleachability of pulps. According to the experience from mills, the gas-off process and the white liquor profiling are effective ways to control extractive and enhance bleachability of RDH pulps [9]. During the pretreatment or pulping, a certain amount of vapor is released out of the digester. This process is called gas-off. A certain amount of cooking white liquor is sent to the pretreatment stage or the post treatment stage. This operation is called white liquor profiling. Therefore, the main objectives of this study is to determine the influence of extractive on the bleachability of pulps prepared from batch extended delignification process. Many reasons account for why some extended delignified kraft pulps are harder to bleach than conventional kraft pulps. The reasons include the natural of the pulps and the operating conditions of the process used during the pulping. It is believed that these factors affect the extractive content of the extended delignified kraft pulps.

In this work, several questions are to be answered:

- (1) What kind of extractives will affect the bleachability of pulp and how?
- (2) How do these extractives distribute during the batch extended delignification process?
- (3) What can be done to modify the extended delignification process to lower the harmful extractive content and improve the bleachability of pulps?

The objectives of this study are:

1. *To determine the role of extractives in ECF (elemental chlorine free) bleaching.* The mechanisms of the extractives influencing the bleachability of kraft pulps will be studied. The reaction and blocking effect of the extractives in both hardwood and softwood kraft pulps will be evaluated. This part focuses on the kinetics of the bleaching process and the effect of extractives as a whole. The reaction of individual extractive compounds will not be studied in details.

2. *To determine how the extended delignification process affects the extractive content of pulps.* The precipitation of extractives on the kraft pulps during the black liquor recycling will be evaluated. How the precipitation process affects the extractive content and bleachability, and how it is affected by the operating conditions will be determined.

3. *To evaluate the possibility of lowering the unsaponifiable extractive content in extended delignified kraft pulps by introducing a gas-off process in the pretreatment.* The influence of pretreatments with the gas-off under different operating conditions on the extractive content and bleachability of both hardwood and softwood kraft pulps will be evaluated.

4. *To investigate the effect of fiber morphology on the bleachability of pulps.* In this part, the effect of the fiber wall thickness on the bleachability of kraft pulps will be briefly evaluated.

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CHAPTER III

Influence of Extractives on the Chlorine Dioxide (ClO₂) Bleaching Process of Kraft Pulps

Abstract

The objective of this part of the research is to study the reactive and blocking effects of extractives in softwood and hardwood kraft pulps during ClO₂ bleaching. Kraft pulps of freshly cut southern pine and southern red oak were prepared from the conventional kraft cooking. These pulps were bleached by ClO₂ and the influence of extractives on the ClO₂ bleaching processes was determined. Extractives consumed some of the ClO₂, which made the kraft pulps with extractives harder to bleach than the extractive-free kraft pulps. Extractives in softwood kraft pulps consumed up to 10% of the ClO₂. Up to 40% ClO₂ was consumed by extractives in hardwood kraft pulps because of the high extractive content and low kappa number. In softwood kraft pulps, due to the thick cell wall, the extractives, both the neutral compounds and the alkaline soluble precipitates, slowed the leaching process of the residual lignin. In hardwood kraft pulps, the blocking effect of extractive was not as significant as in the softwood kraft pulps. The neutral extractives in hardwood kraft pulps mainly contributed to the low leaching rate of the residual lignin. Precipitates had little blocking effect.

Keyword

Bleachability, blocking, chlorine dioxide, extractives, hardwood, kinetics, leaching, kraft pulping, reaction, softwood

Introduction

After kraft pulping, most of the lignin in the wood has been removed by the chemical treatment of kraft cooking. About 5-10% of the natural lignin left in the pulp is carried over to the bleaching process. The purpose of the bleaching processes for kraft pulps is to remove the residual lignin and improve the

brightness of the pulps, while at the same time, preserving the cellulose and hemicellulose. In bleaching, the fiber constituents - cellulose, hemicellulose, residual lignin and extractives - will react with the bleaching chemicals to a varied extent. Many studies have been conducted to investigate the reactions of cellulose, hemicellulose and residual lignin during the bleaching [1,2]. Even though our present knowledge about the structure and reactions of residual lignin, especially about lignin-carbohydrate linkages in kraft pulps, is far from complete, we have had a good overview about the reaction principles of the residual lignin in bleaching [3].

Extractives are minor natural components in the wood and fibers. Their role in determining the pulp bleachability is not as important as that of the residual lignins. Most of the natural extractives will be removed during the kraft pulping by the saponification reactions and micelle formation caused by the presence of resin acids and fatty acids [3, 4, 5]. However, the extractives that are stable enough to survive the pulping process and stay with the pulp will be carried over to the bleaching stages.

In the bleaching process, there are several possible mechanisms by which the extractives affect the bleachability of the pulps. The extractives may react with the bleaching chemicals by the reaction mechanism. They also may interfere the diffusion process by the blocking mechanism. The colored extractives may hurt the final brightness of bleached pulps by the coloring mechanism.

Some of the extractives with unsaturated structures, such as unsaturated fatty acids and resin acids, are extremely reactive toward bleaching chemicals such as Cl_2 , ClO_2 , etc. [6]. Some of the saturated structures in extractives might also be oxidized [7]. A portion of the bleaching chemicals is consumed by these extractives, which lowers the bleaching efficiency of the bleaching chemicals at the same chemical charge.

Some extractives are very inert toward the bleaching chemicals [8]. The surface of unbleached chemical pulps was found to be covered with a higher

concentration of extractive and lignin than in the cell wall by using Electron Spectroscopy for Chemical Analysis (ESCA) (also known as X-ray Photo-Electron Spectroscopy (XPS))[9,10]. This thin layer of extractives decreases surface contact angle, surface energy and polarity of the fiber, and thus increases the hydrophobicity of the fiber [11, 12]. Therefore, the surface extractives may prevent the diffusion of the lignin fragments out of the fiber wall or block the penetration of bleaching chemicals into the fiber wall. In addition to the extractives, the surface lignin, originating from wood fibers or formed during the cooking, is more condensed and less reactive to the bleaching chemicals [10]. They may also affect the pulp bleachability by the blocking mechanism.

Some of the wood species, especially some of the tropic hardwood species, have a high content of colored polyphenolic compounds. These compounds, most of which are tannins and flavonoids, are dominant in heartwoods. Some of these compounds with highly condensed structures can survive the bleaching process and lower the final brightness of pulps [13, 14].

Generally, the kraft pulp of southern softwood has lower extractive content and thicker fiber wall than that of southern hardwood. Due to the thick cell wall, the diffusion process of lignin or bleaching chemicals affected by extractives may be more important for softwood fibers than for the hardwood fibers. For the kraft pulp from hardwood, due to the lower kappa number and relatively higher extractive content, the reaction effect of the extractives is expected to be more important. In this paper, kraft pulps prepared from two southern wood species, loblolly pine and southern red oak were bleached. Kinetic studies were used to investigate the reaction of extractives with ClO_2 and the diffusion of residual lignins. This study focused on the influence of extractives as a whole. The effect and reaction of individual extractive compounds were not investigated in detail.

Experimental

Raw Material

A 30-year old loblolly pine tree and a 30-year old southern red oak tree grown in Raleigh, North Carolina, USA, were used in this study. The wood logs were debarked and then chipped. The chips with around 50% moisture (wet basis) were screened. The accepts with size between 1” and 5/8” slots of the screen and with thickness under 8 millimeter were used. The chips were kept fresh in the refrigerator at 4°C to prevent the loss of extractives. The extractive contents of the wood were determined as following:

Table 3-1. Extractive Content of the Wood

Wood Species	Southern Pine	Southern Red Oak
Total Extractive Content, %	2.47	1.12
Neutral Extractive Content, %	0.17	0.19

Pulping

The Kraft cooks were done in one 7L M&K digester vessel. 1000g oven dry (OD) based chips were used in each cook. The cooking conditions are described in Table 3-2. The target kappa number for the softwood kraft pulp was between 20 and 30. The target kappa number for the hardwood kraft pulp was between 10 and 18.

Table 3-2. Conditions of Kraft Cooking

	Softwood	Hardwood
Active Alkali Charge, as Na ₂ O	19%	16.5%
Sulfidity	25%	25%
Liquor Volume	4.5L	4.0L
Temp Increasing Rate	100°C/hr	100°C/hr
Maximum Temperature	170°C	170°C
Time at Maximum Temp	To desired H-factor	

Bleaching

Bleaching was conducted in high density polyethylene (HDPE) bags by mixing pulps and bleaching chemicals together. These bags were sealed and put into a water bath under 70°C. The bleaching sequence D(E+P)D was used. The operating conditions used during the bleaching are listed in Table 3-3.

Table 3-3. Process Conditions for Bleaching

Stage	Time(mins)	Temp(°C)	Consistency	Chemical Charge	Final pH
D ₀	60	70	10%	K.F. = 0.25	
E+P	60	70	10%	NaOH = 1.5% H ₂ O ₂ = 0.5%	10.3 – 10.9
D ₁	180	70	10%	ClO ₂ = 1.0%	3.5 – 4.0

Extraction and Fractionation

Extractive-free chips and pulps were prepared by soxhlet extraction. The wet samples were put in a 2500 ml soxhlet extractor and at first extracted with acetone to remove most of the water. Then the samples were extracted with ethanol and benzene mixture (1:2 ratio) to remove the extractives. The extracted samples were subsequently extracted with ethanol to remove the benzene. Each

stage of extraction was carried out for at least 12 hrs. Finally, the samples were thoroughly washed with water and immersed in water for at least 24 hours.

To determine the extractive content of wood meal and pulps, samples of wood chips and pulps were dried overnight in a vacuum oven at 45°C. The wood meals were prepared by grinding the wood chips in a Willey mill and sieving through a 40 mesh screen. 20 grams (OD basis) of wood meal and 15 grams of pulp (OD basis) were used. The wood meals and pulps were extracted for at least 10 hrs in a soxhlet with acetone and then with 95% ethanol. The extracted solutions were combined and the solvents were removed by using a rotavapor at 45°C. The extracts were hydrolyzed at 70°C in a 500ml flask for 4 hrs with 80ml 0.5N KOH/95% ethanol solution. Then the solution was diluted with 80ml water and the pH of the solution was adjusted to 13.2 ± 0.2 with KOH. The diluted solution was extracted in a separatory funnel with hexane three times, each with 50ml of hexane. The extractives in hexane phase were labeled as the neutral fraction. Then the water phases were acidified to pH around 2.5 by adding 1N HCl and then extracted in a separatory funnel with chloroform three times, each with 50 ml of chloroform. The extracts were labeled as the saponifiable fraction. The sum of the neutral fraction and the saponifiable fraction was the total extractive content of the sample.

Bleaching Kinetics

Bleaching kinetics was conducted in 1.0 liter PVC bottles. 10 grams of pulp was used in each experiment. The pulp was mixed with ClO₂ solution in the bottle and the bottle was sealed. The bottle was put in the water bath under controlled temperature. The operating conditions are listed as following:

Pulp:	10g
Kappa Factor:	0.25
Consistency:	1%
Temperature:	70°C
Starting pH:	10.5

For the blank case, only water and the corresponding amount of ClO_2 were put into the bottle. For the extractive case, only water, extractives prepared from 10g of the original pulp and the corresponding amount of ClO_2 were put into the bottle. The kinetic measurements were carried without pulp.

After a period of time, the bottle was taken out of the water bath, quenched with icy water and the residual ClO_2 was titrated. The brightness and the kappa number of the pulp from a parallel bleaching reaction were determined.

Leaching

Leaching measurements were conducted in 1.0 liter PVC bottles. 10 grams of pulp were used in each experiment. The pulp was mixed with NaOH solution in the bottle and the bottle was sealed. The bottle was put in a water bath under controlled temperature. The operating conditions are listed as following:

Pulp:	10g
NaOH Charge:	0.01 M
Consistency:	1%
Temperature:	70°C
Starting pH:	11.8

After a period of time, about 15 ml solution was taken out from the bottle by a syringer. The solution was cooled down to the room temperature and filtered. The amount of lignin dissolved during the alkaline treatment was measured by UV at 280nm using a molecular extinction coefficient of 20l/g-cm[15]. Leachability measures the diffusion rate of the bulky lignin out of the fiber wall. Since the extractive molecules are smaller than lignin molecules, they are much easier to leach. Some of the extractives have absorbance at 280nm. Therefore, the existence of extractives will affect the accuracy of the lignin leaching measurement. To exclude the effect of extractives, the leaching data of

pulps with extractives was adjusted by subtracting the absorbance at 280nm of only extractives in the same alkaline solution.

The lignin content of pulps before and after the leaching was determined from the kappa number analysis. Since extractives may contribute to 1-2 units to the total kappa number, the leachability of lignin is influence by the existence of extractives. To exclude the effect of extractives, before or after the leaching experiment, all pulp samples were extracted by organic solvents and the kappa number of the extracted pulp was measured.

Results and Discussion

Section I. Softwood Kraft Pulps

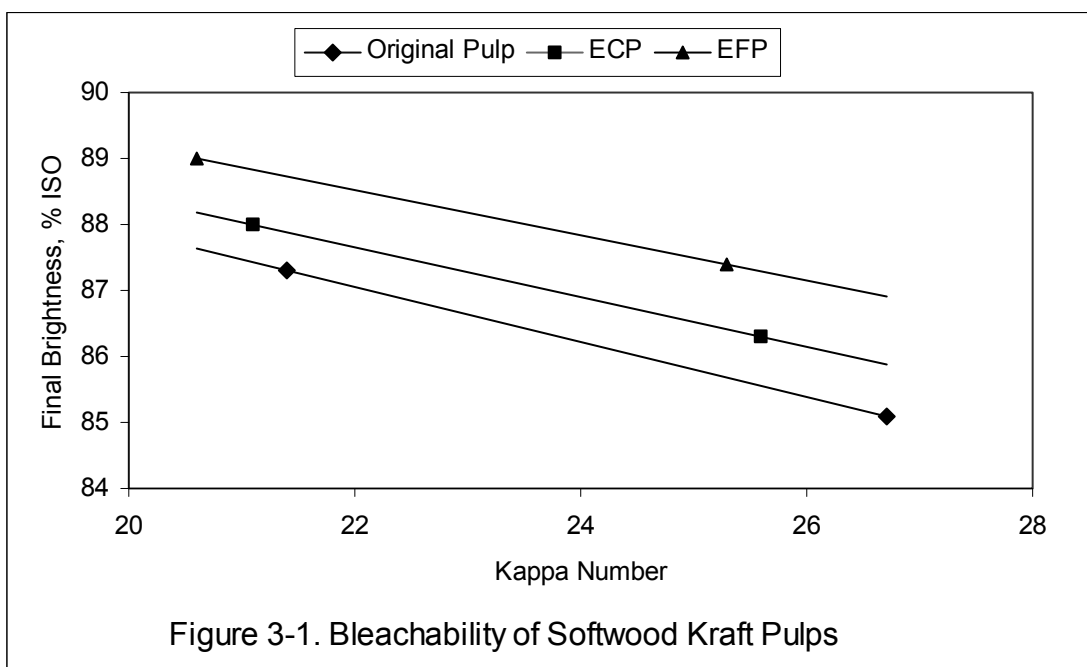
Extractive Content and Bleachability of Kraft Pulps

The total extractive content and the neutral extractive content of softwood kraft pulps are listed in Table 3-4. “Original pulp” is the kraft pulp prepared from the original, untreated chips. “Extracted chip” refers to the kraft pulp prepared from the treated chips after the organic solvent extraction, and is labeled as ECP. “Extracted pulp (EFP)” is the original pulp after the organic solvent extraction. “Extractives + extracted pulp” refers to the mixture of extractives and the extracted pulp. It was prepared by extracting the original pulp to separate the extractives and the fibers. Then the extractive-free pulp and the extractives were mixed together mechanically. The mixture was labeled EEP.

Table 3-4. Extractive Content of Conventional Kraft Pulps (Kappa = 21)

	Total Extractive Content,%	Neutral Extractive Content,%
Original Pulp	0.64	0.27
Extracted Chip(ECP)	0.34	< 0.01
Extracted Pulp(EFP)	< 0.01	< 0.01
Extractives+Extracted Pulp(EEP)	0.11	< 0.01

For ECP, all the extractives were removed prior to the kraft cooking. Therefore, the neutral extractive content in ECP was undetectable. The total extractive content of ECP was about a half of the extractive content of the original pulp. Almost all the extractives in ECP were the precipitates from the black liquor during the kraft cooking and they are soluble in alkaline solution. For EFP, all the neutral extractives and alkaline soluble extractives were removed by organic extraction. The extractive content in EFP was undetectable. By mixing extractives and the extracted pulp together, about one sixth of the total extractives were adsorbed by the fiber during the mixing process (Table 3-4). Almost all the adsorbed extractives were alkaline soluble and the neutral extractive content in EEP was undetectable.



The bleachabilities of the original pulp, ECP and EFP are shown in Figure 3-1. After extraction of the chips, almost all the neutral compounds and most of the saponifiable compounds were removed. The bleachability of ECP was higher

than that of the original pulp. After extraction of the pulps, not only the natural extractives originated from the chips, but also some of the surface lignin and other precipitates generated during the kraft pulping were removed. Therefore, the bleachability of EFP was further enhanced.

ClO₂ Bleaching Kinetics

The kinetics of kraft pulps bleached by ClO₂ is shown in Figure 3-2. It was indicated by the residual ClO₂ that the extractives did react with ClO₂ at the very beginning of the bleaching stage. However, compared to the reaction of the residual lignin with ClO₂, the ClO₂ consumed by extractives in softwood was only a minor fraction. Less than 10% of the ClO₂ was consumed by extractives. From the kappa number and brightness of the kraft pulps after bleaching, it's easy to understand that the bleachability of ECP and EFP were higher than that of the original pulp. In the EEF mixture, all the extractives contained in the original pulp were present in this mixture. The only difference from the original pulp was the distribution of the extractives. In EEP, about one sixth of the extractives was absorbed by the surface of the pulp. Five sixths of the extractives, including almost all the neutral extractive compounds, stayed in the filtrate after mixing. The extractive content inside the fiber wall was negligible. If the difference in the bleachability between the original pulp and the extracted pulp were totally due to the reaction of extractives with ClO₂, the EEP should have the same bleachability as the original pulp. Kinetic results indicated, however, that the bleachability of EEP was higher than that of the original pulp, which implied that the distribution of extractives did affect the bleachability of pulps. If all the extractives stay within the fiber instead of outside the fiber, the extractives may block the penetration of bleaching chemicals and retard their reactions with the residual lignin.

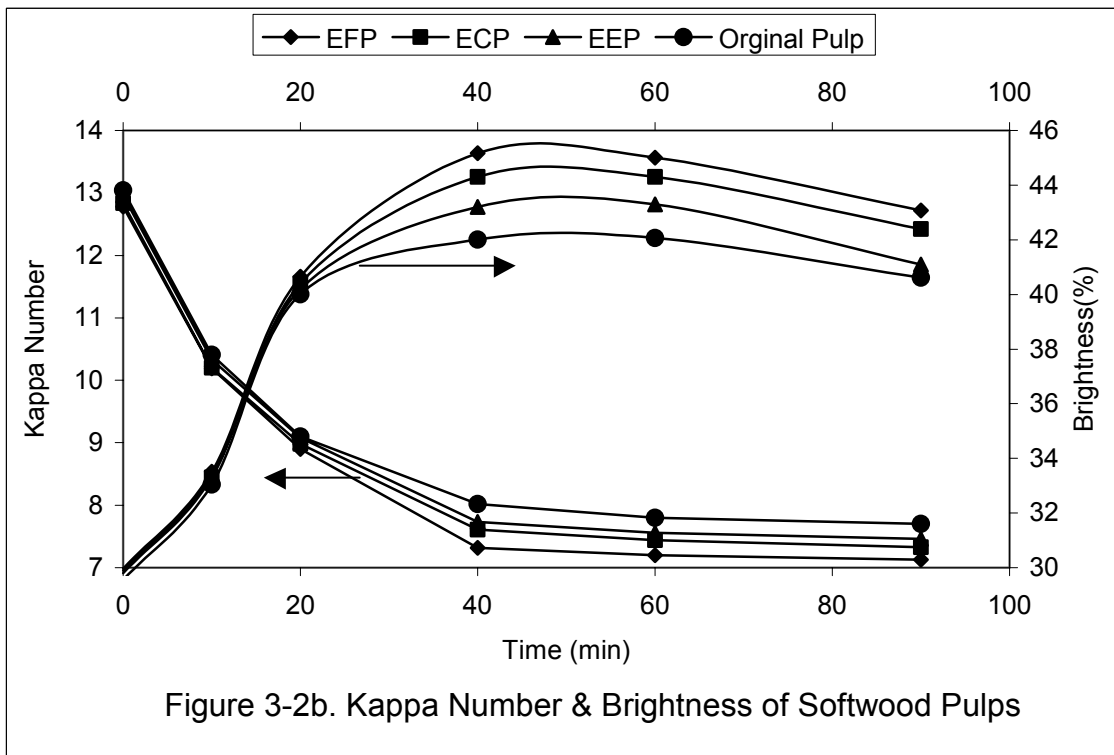
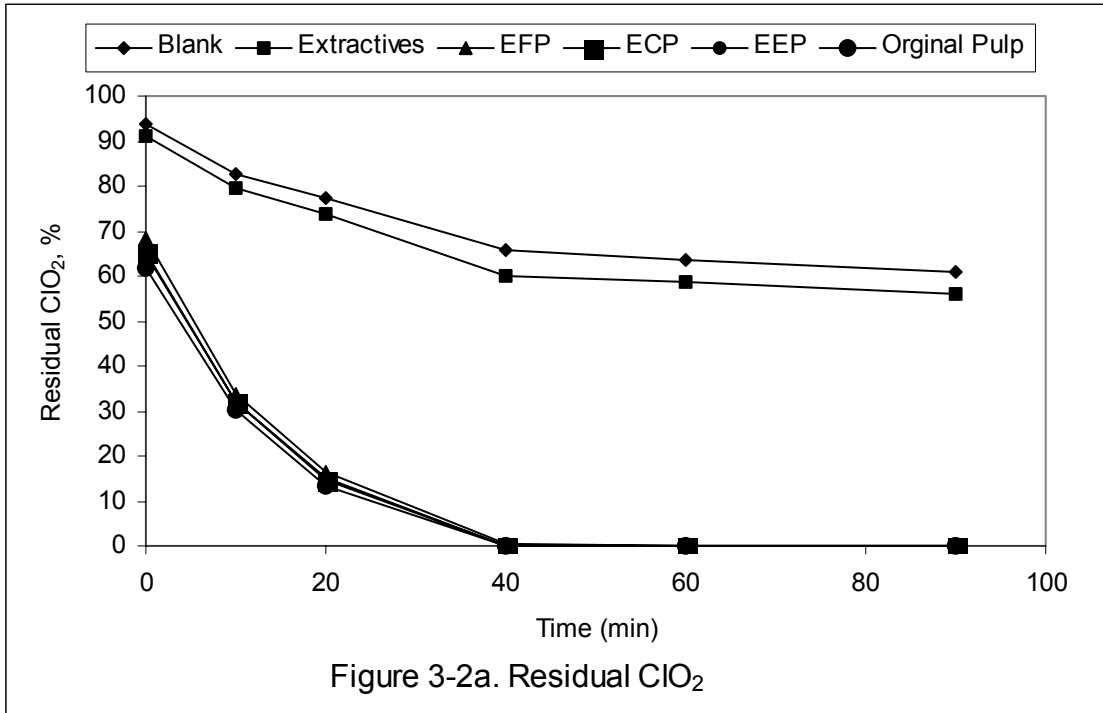
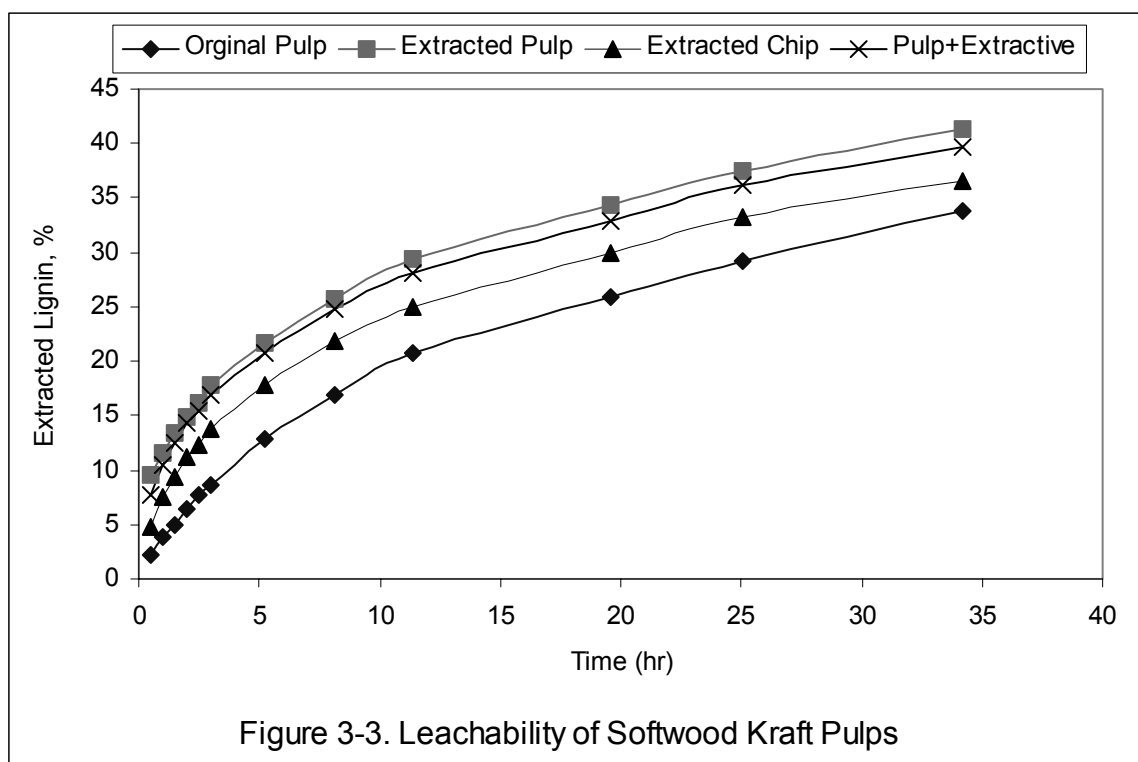


Figure 3-2. Kinetics of Softwood Kraft Pulps Bleached with ClO₂

Leachability of Kraft Pulps

The leachability measures the rate of the residual lignin diffusing out of the fiber. The leachability of the kraft pulps measured by UV is shown in Figure 3-3. EFP and EEP had higher leachability than the original pulp, which was due to the lower blocking effect of the extractives. ECP had lower leachability than EFP. The neutral extractives were undetectable in ECP, and most of the extractives in ECP were precipitates generated during kraft pulping. This indicated that the surface lignin and precipitates in ECP could block the diffusion of lignin or bleaching chemicals, which may be due to their more condensed structure, lower reactivity and high hydrophobicity.



The amount of residual lignin left in the kraft pulps after leaching was indicated by the kappa number of the pulps. Table 3-5 shows the kappa number

of the kraft pulps before and after 90 minutes of leaching. The kappa numbers were adjusted by excluding the extractives.

Table 3-5. Kappa Number of Kraft Pulps before and after Leaching

	Before Leaching	After Leaching
Original Pulp	25.9	22.7
ECP	25.4	21.6
EFP	26.0	21.8

The difference in kappa number between before leaching and after leaching was 3.2, 3.8 and 4.2 for the original pulp, ECP, and EFP, respectively. The lower amount of lignin leached in the original pulp and ECP than in EFP further indicated that the extractives, including the natural extractives and precipitates from the kraft cooking, blocked the diffusion process of the residual lignin during the bleaching.

Section II. Hardwood Kraft Pulps

Extractive Content and Bleachability of Kraft Pulps

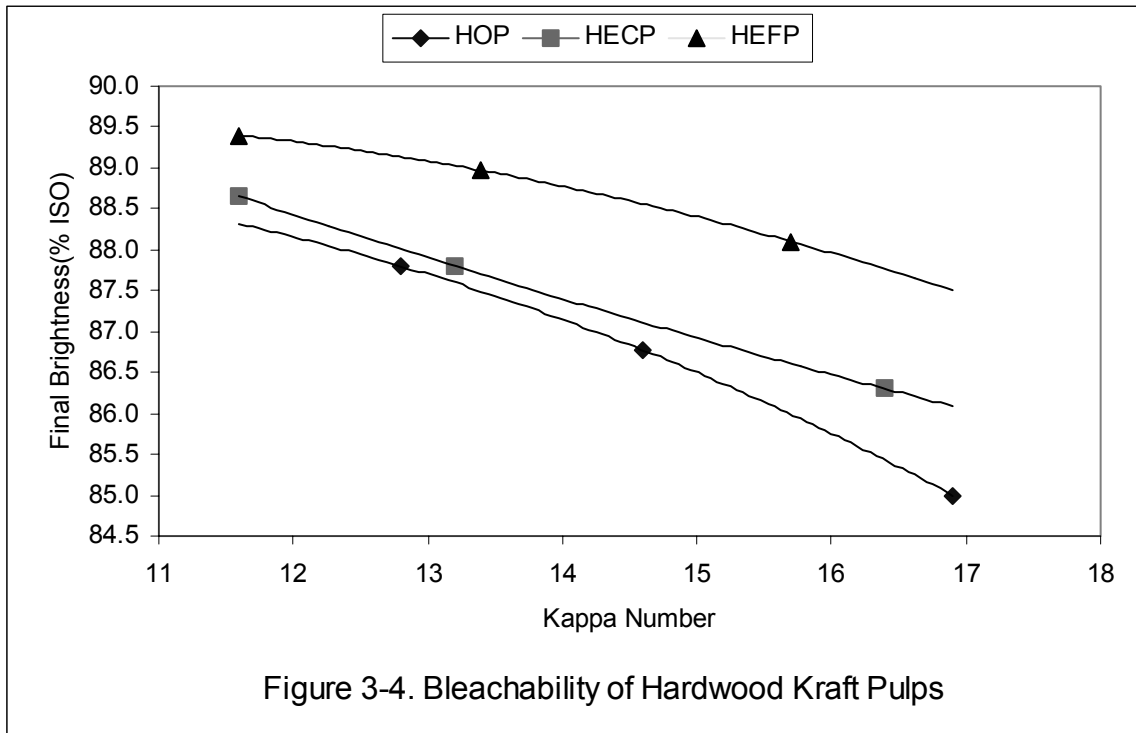
The total extractive content and neutral extractive content of hardwood kraft pulps are listed in Table 3-6. The original pulp, the kraft pulp prepared from the treated chips after organic solvents extraction, the extracted pulp and the extractives-extracted pulp mixture were labeled as HOP, HECP, HEFP and HEEP respectively.

Table 3-6. Extractive Content of Conventional Kraft Pulps

	Total Extractive Content, %	Neutral Extractive Content, %
Original Pulp(HOP)	0.66	0.38
Extracted Chip(HECP)	0.41	< 0.01
Extracted Pulp(HEFP)	< 0.01	< 0.01
Extractives+Extracted Pulp(HEEP)	0.19	0.07

Similar to softwood kraft pulps, the neutral extractive content in HECP was undetectable and the total extractive content of HECP was a little more than half of the extractive content of the original pulp. By removing all the natural extractives before cooking, almost all the extractives in HECP were the precipitates from the black liquor during the kraft cooking and they were soluble in alkaline solutions. For HEFP, all the neutral extractives and alkaline soluble extractives were removed by the organic extraction. In the mixture HEEP, about one fourth of the total extractives and one fifth of the neutral extractives were adsorbed by the fiber during the mixing process (Table 3-6).

The bleachability of the original pulp, HECP and HEFP are shown in Figure 3-4. Also very similar to softwood kraft pulps, after extraction of the chips, almost all the neutral compounds and most of the saponifiable compounds were removed. The bleachability of HECP was higher than that of the original pulp. After extraction of the pulp, the bleachability of HEFP was further enhanced.



ClO₂ Bleaching Kinetics

The kinetics of hardwood kraft pulps bleached by ClO₂ is shown in Figure 3-5. The extractive content in hardwood kraft pulps is generally higher than that in softwood kraft pulps. The kappa number of the conventional hardwood kraft pulps is much lower than that of softwood kraft pulps. Therefore, the extractive content per kappa number of the hardwood kraft pulp is much higher than that of the softwood kraft pulps. The bleaching chemical charge is usually based on the kappa number of the kraft pulp. At the same ClO₂ charge, i.e., same kappa factor, it is generally expected that the extractives in the hardwood kraft pulp consume more ClO₂ than in the softwood kraft pulp. Indicated by the amount of residual ClO₂, more ClO₂ was consumed by the extractives in hardwood kraft pulps than by the extractives in softwood kraft pulps. In Figure 3-5a, up to 40% of the ClO₂ was consumed by extractives in the hardwood kraft pulp. Figure 3-5b shows that after one hour of ClO₂ bleaching, the kappa number of HEFP was about 1 unit lower than that of HOP. The brightness of HEFP was also about 5%

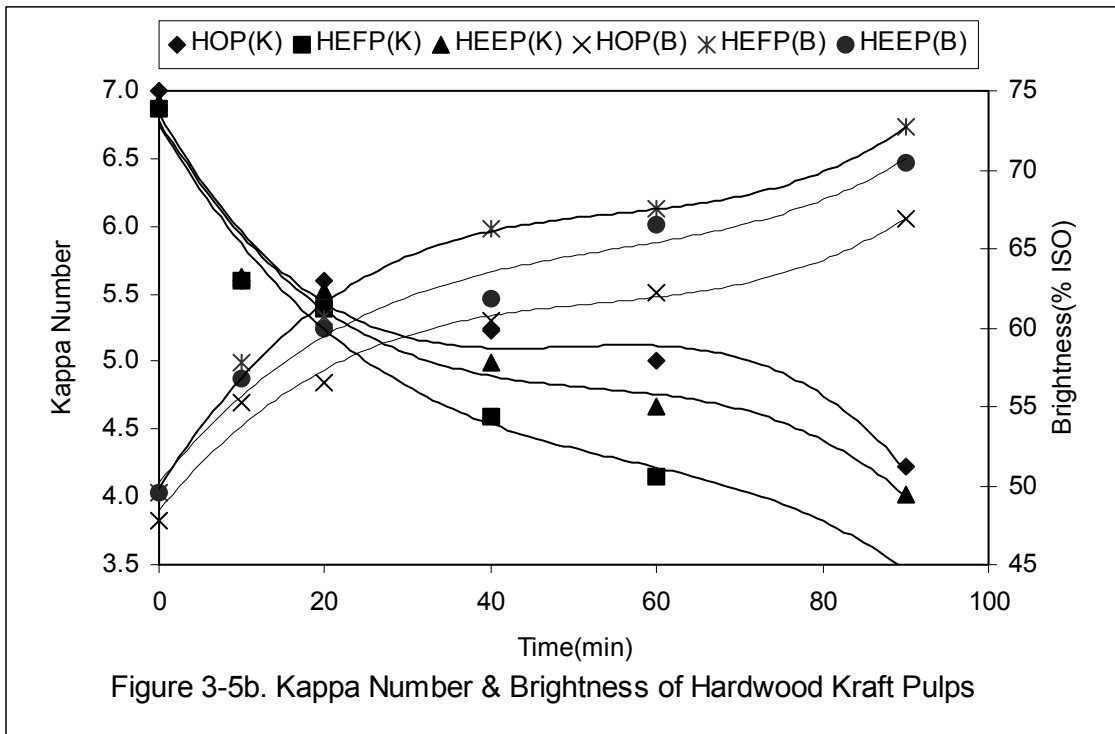
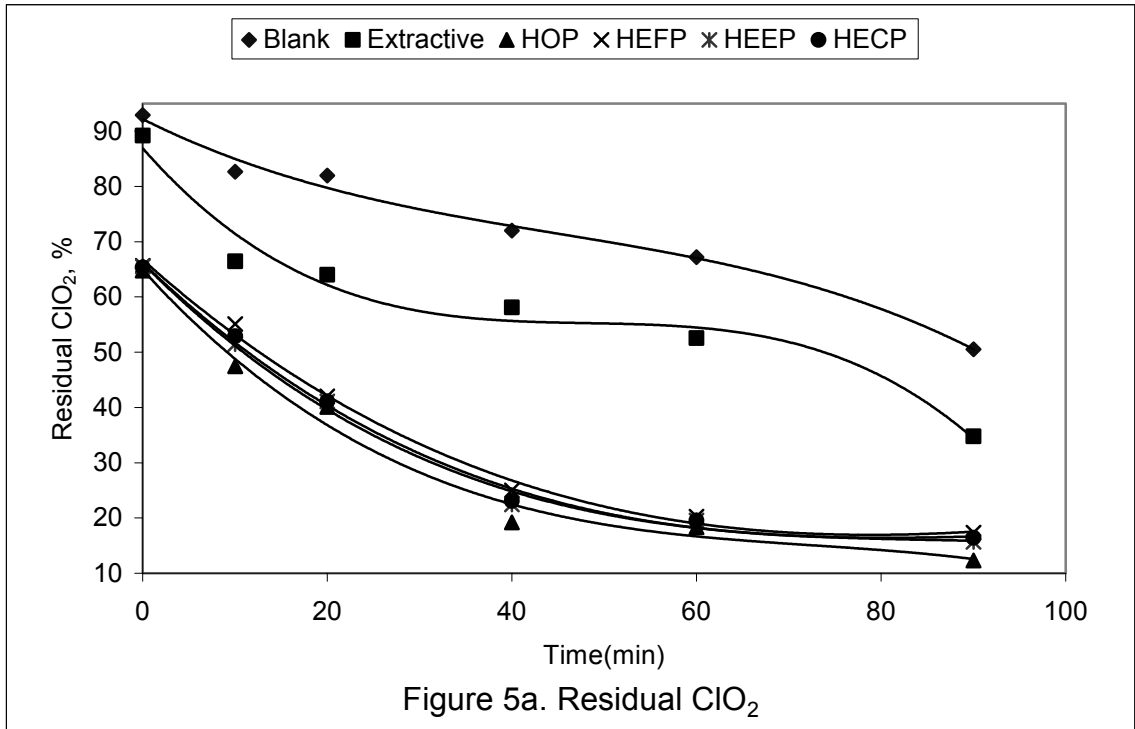
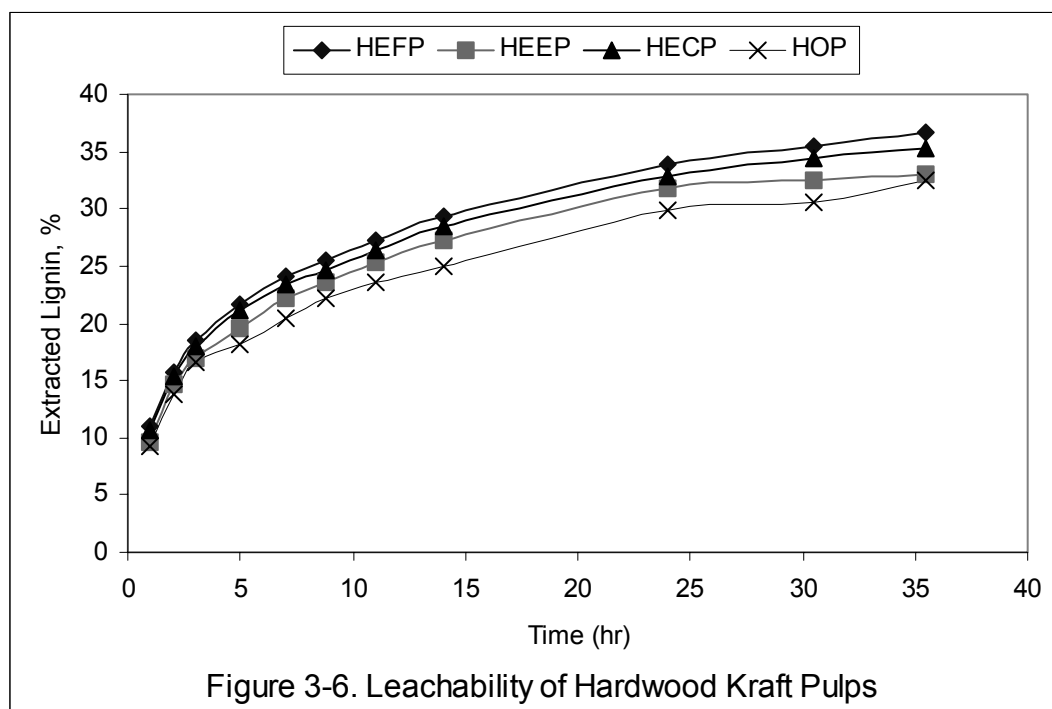


Figure 3-5. Kinetics of Hardwood Kraft Pulps Bleached with ClO₂

ISO higher than that of HOP. This phenomenon indicated that unequal amounts of residual lignin were oxidized by ClO_2 . Less lignin was oxidized in HOP than in HEFP during the same bleaching time. The slower reaction rate in HOP was partially due to the consumption of ClO_2 by extractives. The blocking effect of extractives may also contribute to the slowdown of the residual lignin reaction. The kappa number and brightness of HEFP were between those of HOP and HEFP, which implied that the distribution of extractives affected the ClO_2 bleaching kinetics.

Leachability of Hardwood Kraft Pulps

The leachability of the hardwood kraft pulps measured by UV is shown in Figure 3-6. Even through the cell wall of hardwood fibers was much thinner than that of softwood fibers, the extractives did affect the leaching process of the residual lignin. After 35 hrs of leaching, there was 3-4% difference in the amount of lignin leached between HOP and HEFP. However, the difference was much lower than the corresponding softwood cases, which had an 8% difference.



Similarly, the amount of residual lignin left in the hardwood kraft pulps after leaching was indicated by the kappa number of the pulp. Table 3-7 shows the kappa number of the kraft pulps before and after 90 mins of leaching.

Table 3-7. Kappa Number of Kraft Pulps before and after Leaching

	Before Leaching	After Leaching
HOP	11.6	10.3
HECP	11.9	10.1
HEFP	11.5	9.6

The difference of kappa number of HOP, HECP, and HEFP between before leaching and after leaching was 1.3, 1.8, and 1.9, respectively. The lower amount of lignin leached in HOP than in HEFP further indicated that the extractives in hardwood fiber blocked the diffusion process of the residual lignin during bleaching. However, the residual lignin in HECP and HEFP had almost the same leaching rate. The extractives in HECP had little contribution to the blocking effect. All the extractives in HECP were precipitates during the kraft pulping. Therefore, the slower leaching rate in HOP may be mainly due to the high neutral extractive content in hardwood kraft pulps.

The kraft pulp of southern softwood is difference from that of southern hardwood in that the fiber wall is thicker and the extractive content is lower. Due to the thick cell wall, the diffusion process of lignin or bleaching chemicals affected by extractives was more dominant for softwood fibers than for the hardwood fibers. The reaction of extractives with bleaching chemicals for softwood kraft pulps played a minor role in determining the pulp bleachability due to the high kappa number and relatively low extractive content. For the kraft pulp from hardwood, due to the low kappa number and relatively high extractive content, the reaction effect of the extractives was dominant. Because of the thin

cell wall for the hardwood kraft pulp, the extractives had a small effect in blocking the diffusion process of lignin or bleaching chemicals.

Conclusion

The extractives in southern softwood and southern hardwood conventional kraft pulps affected the bleachability of the kraft pulps. Extractives influenced the ClO₂ bleaching process by reaction and blocking mechanisms.

- Extractives consumed some of the bleaching chemicals by reaction. In softwood kraft pulps, up to 10% of the ClO₂ was consumed by extractives. In hardwood kraft pulps, up to 40% of the ClO₂ was consumed by extractives.
- Extractives in both softwood and hardwood kraft pulps affected the leaching process of the residual lignin possibly by blocking the diffusion of the bleaching chemicals and the residual lignin. In softwood, both the neutral extractive compounds and precipitates during cooking had blocking effects. In hardwood, the extractives had comparatively smaller blocking effects.

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CHAPTER IV

PRECIPITATION OF EXTRACTIVES ONTO KRAFT PULPS DURING BLACK LIQUOR RECYCLING IN EXTENDED DELIGNIFICATION PROCESS

Abstract

The objective of this part is to study the extractive content and the bleachability of the batch extended delignified kraft pulps during the black liquor recycling. Extractives accumulated in the black liquor during the black liquor recycling. Some of the extractives in the black liquor precipitated on the pulps in the pretreatment stage, which affected the bleachability of pulps. For softwood, after 5 stages of black liquor recycling, the extractive content of the kraft pulps increased by up to 4 times and the final brightness decreased up to 2.4% ISO. The amount of extractives precipitating on the pulps strongly depended on the final pH of the pretreatment black liquor, which were determined by the operating conditions such as sulfidity, alkali charge and pretreatment temperature. High alkalinity and low pretreatment temperature was the most efficient combination to minimize extractives from precipitating, and to maintain high bleachability of the kraft pulps. For hardwood, large amounts of extractives precipitated onto fibers, and the extractive content, especially the neutral extractive content, of the hardwood kraft pulps was high. During the black liquor recycling, the drop of the final brightness of hardwood kraft pulps was larger than that of the softwood kraft pulps.

Keyword:

Alkalinity, black liquor, bleachability, extended delignification, extractives, hardwood, kraft pulping, precipitation, pretreatment, recycling, softwood, sulfidity

Introduction

Due to the pressure of the environmental regulations, many technologies have been developed to extend the delignification process in the conventional kraft pulping to lower the residual lignin content without dramatically hurting the strength of the kraft pulps. These well-known extended delignification processes, including Modified Continuous Cooking (MCC)[1], Extended Modified Continuous Cooking(EMCC)[2], Isothermal Cooking(ITC)[3], SuperBatch[4], Lo-Solids[5] and Rapid Displacement Heating(RDH)[6], have been applied in the industry. Some of these processes include a black liquor impregnation stage. The black liquor pretreatment is used to neutralize the acidic groups in the wood [7], save heat energy in warming the chips and improve the selectivity of subsequent kraft cooking [8].

Besides the residual lignin content, the extractives in kraft pulps also affect the bleachability. Extractives are minor natural components of the wood. Most of the extractives are removed during the kraft pulping by the saponification reactions and micelle formation [9, 10]. During the time scale of the kraft pulping, about 80-85% of the extractives dissolved in the black liquor [11]. However, at the end stage of the pretreatment or cooking, due to the negative effects of lignin repolymerization and/or condensation reactions, lignin fragments are more condensed and hydrophobic [12]. Therefore, they may precipitate from the black liquor and be adsorbed by the fiber surface. When the alkali concentration of the black liquor is low, it is easier for extractives and lignin fragments to precipitate on the fiber surface than in the higher alkali concentration liquor. The fiber surface of unbleached kraft pulps was found to be covered with a higher concentration of extractives [13] and lignins [14] than inside the fiber wall by using Electron Spectroscopy for Chemical Analysis (ESCA). This layer of organic compounds, either originating from wood fibers or forming during the kraft cooking, were more condensed and more inert toward bleaching chemicals. They retarded the bleachability of the pulp [14].

Almost all batch extended delignification systems, such as RDH, SuperBatch and Enerbatch, involve at least one stage of black liquor

impregnation [15]. The black liquor used in the pretreatment is recycled from the previous cooks and reused. During the recycling, lignin fragments and extractives accumulate in the black liquor. Therefore, when the extractive content in the black liquor is very high and the pH of the black liquor is low, some of them may be adsorbed by the fiber surface. It was found that the contact time of the pulp with the black liquor during pulping was a factor influencing the bleachability of the pulp [16]. This may make the extended delignified kraft pulps harder to bleach than the conventional kraft pulps. Previous study has shown that the hardwood pulps cooked by the RDH process were harder to bleach when compared with the kraft-O₂ pulps [17]. Pulps produced from low-dissolved-solid liquors had an average brightness of 10 units higher than those produced from high-dissolved-solid liquors [18].

In this study, the behavior of the extractives precipitating on the fiber during the black liquor recycling in batch extended delignified kraft cooks was studied. A simplified extended delignification process, with one stage of black liquor pretreatment and no post treatment, was used in this study. The influence of the following factors on the extractive content and bleachability of softwood kraft pulps during 5 stages of black liquor recycling was studied: 1) sulfidity of the black liquor, 2) alkalinity, 3) pretreatment temperature. For comparison, the effect of the black liquor recycling in the hardwood extended delignification process was also described.

Experimental

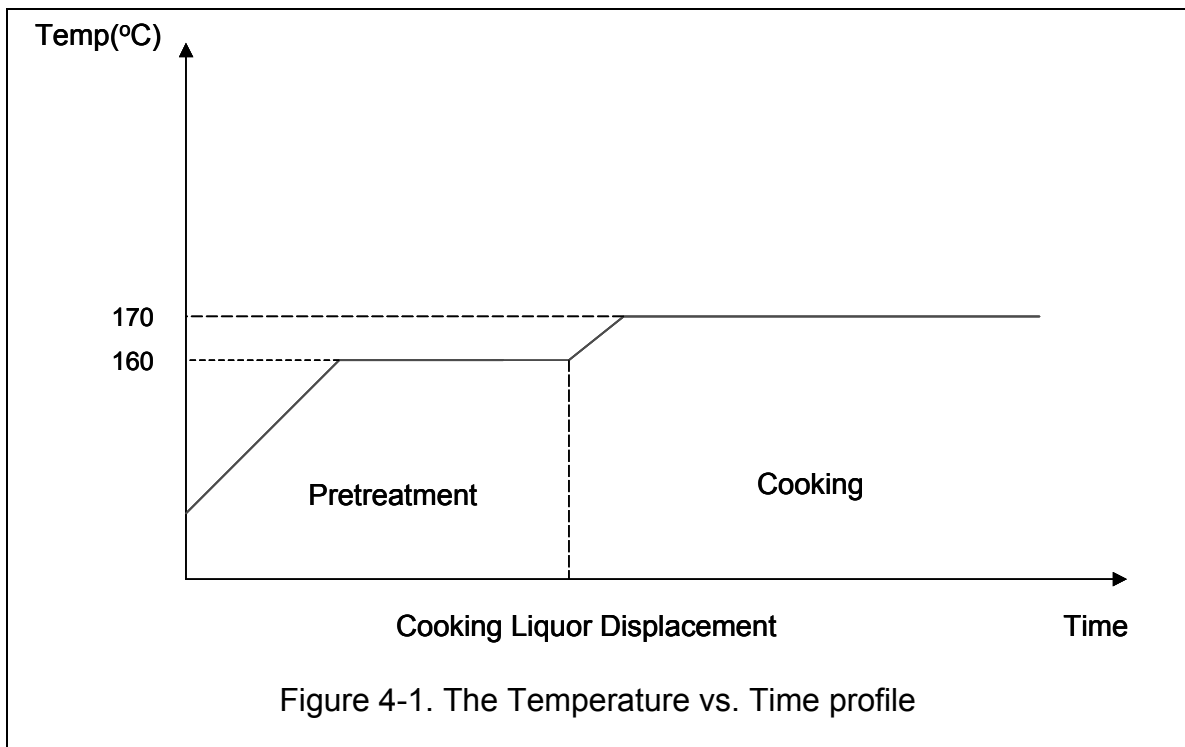
Raw Materials

A 30-year old loblolly pine tree and a 30-year old southern red oak tree grown in Raleigh, North Carolina, USA, were used in this study. The wood logs were debarked and chipped. The chips with around 50% moisture content (wet basis) were screened. The accepted fraction with the size between 1" and 5/8" and with the thickness under 8 mm was used. The chips were kept fresh in the refrigerator at 4°C to prevent the loss of extractives. The extractive contents of the wood were determined as listed in Table 4-1.

Table 4-1. Extractive Content of the Wood

Wood Species	Southern Pine	Southern Red Oak
Total Extractive Content, %	2.47	1.12
Neutral Extractive Content, %	0.17	0.19

Pulping



A simplified extended delignification process, with one stage of black liquor pretreatment and no post treatment, was used. The extended kraft cooks were done in two 7L M&K digester vessels. One was used as the digester and the other was used as the liquor accumulator. 1000 grams of oven dried (OD) based chips were used in each cook. The temperature vs. time profile of the cook is outlined in Figure 4-1. In the pretreatment stage, the wood chips were

impregnated with black liquors. The temperature of the pretreatment stage was increased to a given temperature (160°C or 130°C) and kept for a period of time. The total treating time for the whole pretreatment stage was kept for 100 minutes. At the end of the pretreatment, the preheated cooking white liquor (2.5 liter) was transferred to the digester to displace 2.5L of the pretreatment black liquor. Then the temperature of the system was heated up to 170°C and kept at 170°C to the desired H-factor. The target kappa number for the softwood pulps was 24 and for the hardwood pulps was 9. The cooking conditions are described in Table 4-2a and 4-2b.

Table 4-2a. Conditions of Extended Kraft Cooking for Softwood

	Pretreatment Stage	Cooking Stage
Active Alkali Charge, as Na ₂ O	7.5 – 12 %	21%
Sulfidity	25 – 60 %	25%
Liquor Volume	4.5L	2.5L Cooking WL
Temp Increasing Rate	100°C/hr	100°C/hr
Maximum Temperature	130 – 160°C	170°C
Time at Maximum Temp	20 – 40 minutes	To desired H-factor

Table 4-2b. Conditions of Extended Kraft Cooking for Hardwood

	Pretreatment Stage	Cooking Stage
Active Alkali Charge, as Na ₂ O	11 %	18%
Sulfidity	60 %	25%
Liquor Volume	4.5L	2.5L Cooking WL
Temp Increasing Rate	100°C/hr	100°C/hr
Maximum Temperature	160°C	170°C
Time at Maximum Temp	20 minutes	To desired H-factor

Under each set of conditions, 5 stages of the black liquor recycling were conducted. In the first stage, white liquor was used in the pretreatment. In the following stages (2nd – 5th), 3 liters of the black liquor collected from the previous stage of cooking was used in the pretreatment. In each stage, the active alkali charge and sulfidity of the liquor at the very beginning of the pretreatment were kept exactly the same. 2.5 liter of white liquor was used as the cooking white liquor in all stages and it was preheated to 160°C before transferring.

The dissolved solid content of the pretreatment black liquor was measured by drying the black liquor in the oven at 105°C. The organic solid content of the dissolved solids in the black liquor was measured by burning the organics in a muffle furnace at 500°C.

Bleaching

Bleaching was conducted in high density polyethylene(HDPE) bags by mixing pulps and bleaching chemicals together. These bags were sealed and put into a water bath set at 70°C. The bleaching sequence D(E+P)D was used. The operating conditions used in the bleaching are listed in Table 4-3. The final brightness of the pulp was measured according to the ISO standard.

Table 4-3. Process Conditions for Bleaching

Stage	Time(mins)	Temp(°C)	Consistency	Chemical Charge	Final pH
D ₀ (Softwood)	60	70	10%	K.F. = 0.25	
D ₀ (Hardwood)	60	70	10%	K.F. = 0.20	
E + P	60	70	10%	NaOH = 1.5% H ₂ O ₂ = 0.5%	10.3 – 10.9
D ₁	180	70	10%	ClO ₂ = 1.0%	3.5 – 4.0

Extraction and Fractionation

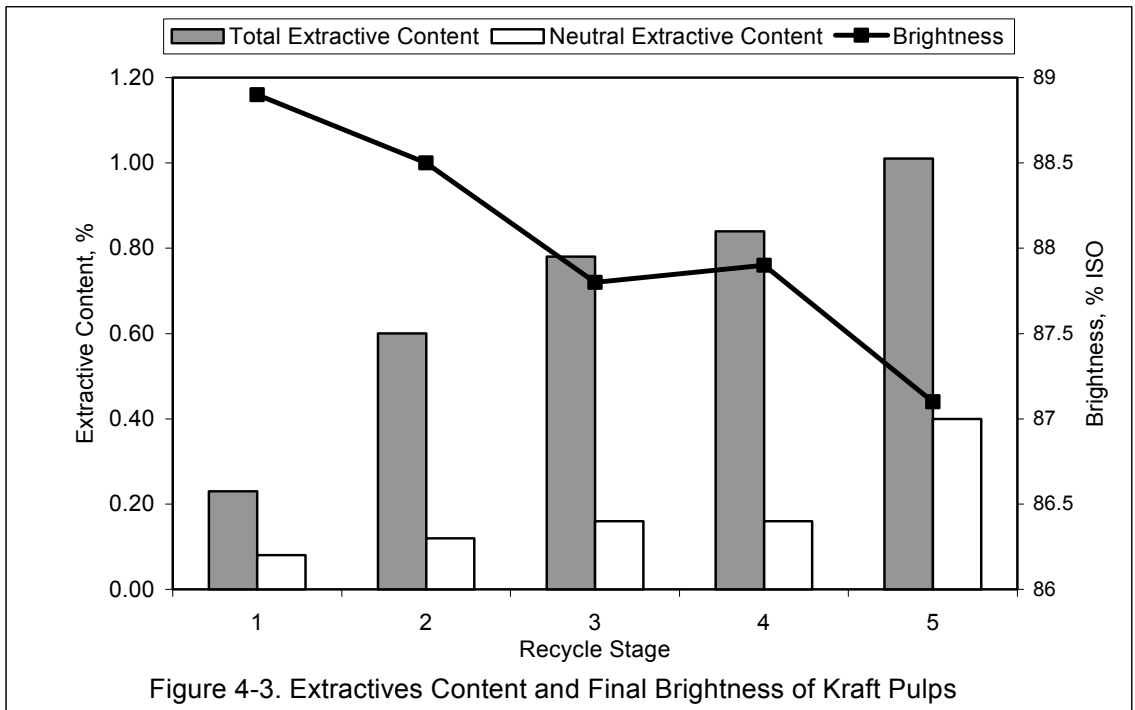
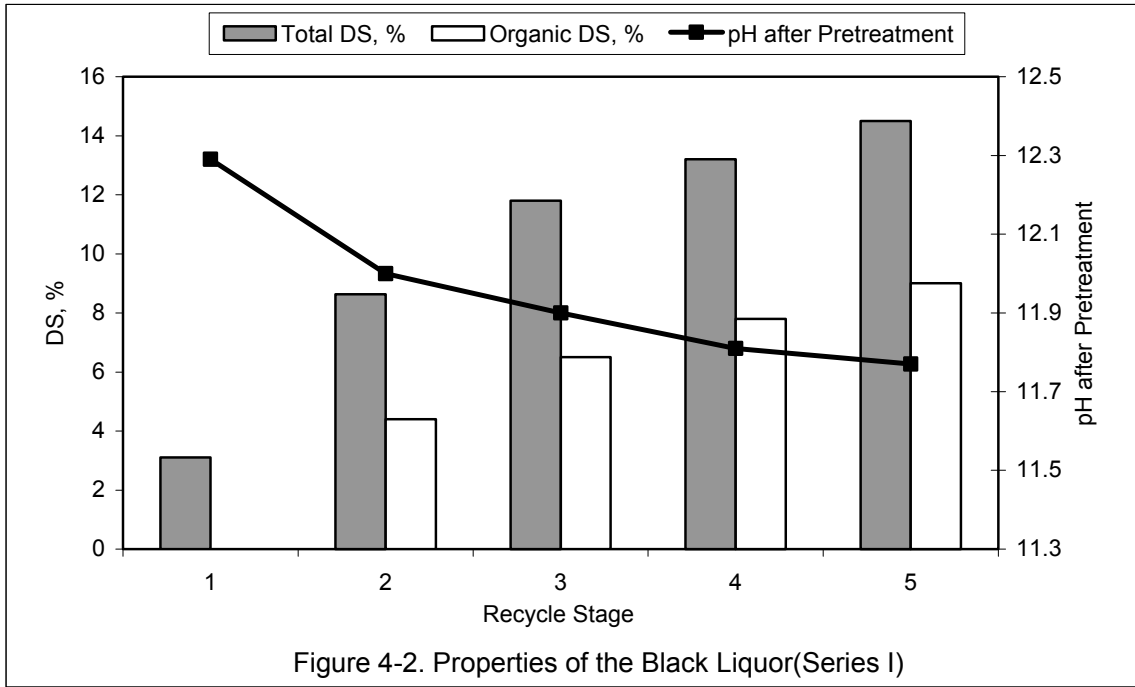
To determine the extractive content of the wood meal and the pulp, samples of wood chips and pulps were dried overnight in a vacuum oven at 45°C. The wood meals were prepared by grinding the wood chips in a Willey mill and sieving through a 40 mesh screen. 20 grams of wood meal (OD basis) or 15 grams of pulp (OD basis) was extracted for at least 10 hrs in a soxhlet with acetone and then with 95% ethanol. The solutions after extraction were combined and the solvents were removed by using a rotavapor at 45°C.

The extracts were hydrolyzed at 70°C in a 500 ml flask for 4 hours with 80ml 0.5N KOH/95% ethanol solution. Then the solution was diluted with 80 ml water and the pH of the solution was adjusted to 13.2 ± 0.2 by KOH. The diluted solution was extracted in a separatory funnel with hexane three times, each with 50ml of hexane. The extractives in the hexane phase were labeled as the neutral fraction. Then the water phases were acidified to pH around 2.5 by adding 1N HCl and extracted in a separatory funnel with chloroform three times, each with 50ml of chloroform. The extractives in chloroform were labeled as the saponifiable fraction. The sum of the neutral fraction and the saponifiable fraction was the total extractive content of the sample.

Results and Discussion

Series I:

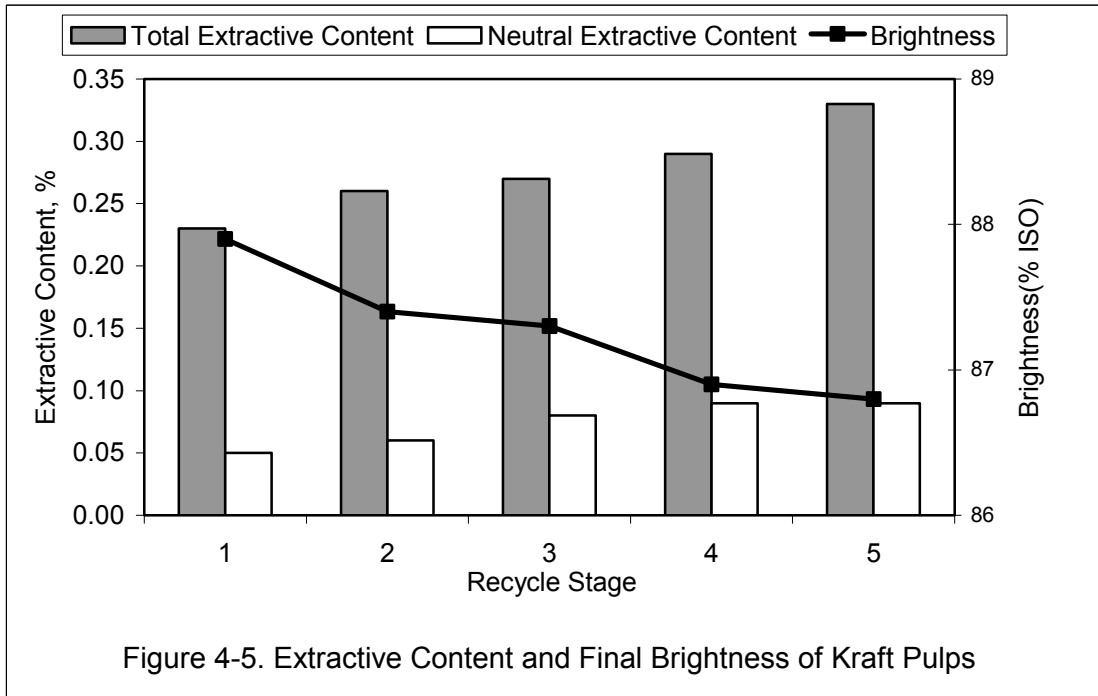
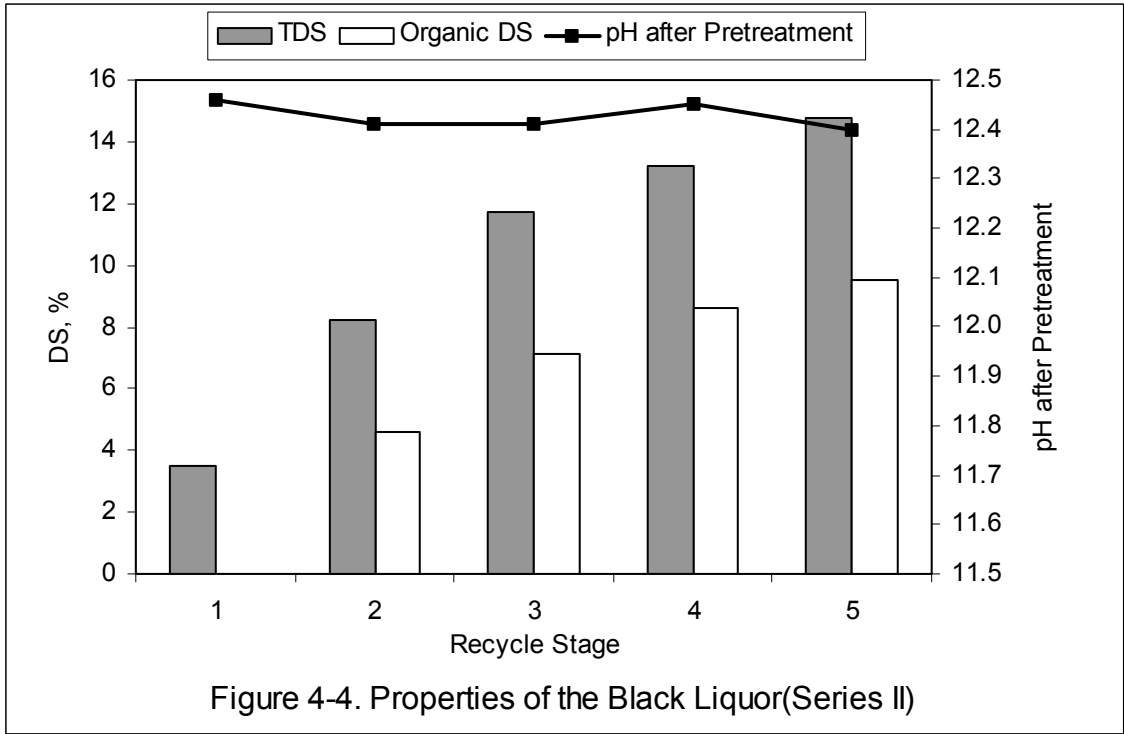
In this series, softwood chips were used. In the pretreatment, the initial active alkali charge was 11% and the sulfidity was 60%. Figure 4-2 shows the dissolved solid content of the pretreatment black liquor before the pretreatment and the pH value of the black liquor after the pretreatment. After 5 stages of the black liquor recycling, the total dissolved solid (TDS) content and the organic dissolved solid (ODS) content in the pretreatment black liquor increased very quickly. The pH value of the black liquor after the pretreatment decreased after each stage of black liquor recycling. The OH⁻ concentration in the fifth stage was decreased to as much as 30% of that in the first stage.



The properties of the kraft pulps are shown in Figure 4-3. The extractive content in the pulps built up very quickly. After 5 stages of the black liquor recycling, the total extractive content in the pulp was almost 5 times as much as that in the first stage. The neutral extractive content was also increased by almost 4 times. The final brightness of the bleached pulps dropped by 2% ISO after 5 stages of recycling. During the black liquor recycling, more and more extractives accumulated in the black liquor. When the pH of the black liquor dropped, it was easier for the extractives to precipitate onto the fiber surface.

Series II.

In this series, softwood chips were used. In the pretreatment, the active alkali charge was 11% and the sulfidity was decreased to 25% at the beginning of the pretreatment in each stage. The properties of the black liquor and kraft pulps are shown in Figure 4-4 and 4-5, respectively. Though the TDS and ODS in the black liquor increased rapidly after 5 stages of black liquor recycling, the extractive content of the kraft pulps had only a small increase, 40% for the total extractive content and 70% for the neutral extractive content. The final pH of the black liquor remained almost constant at 12.4 during the black liquor recycling. The tendency for extractives to precipitate during the black liquor recycling had only a small change. Due only to the high concentration of extractives in the black liquor during recycling did the extractive content of the kraft pulps increase. The final brightness was only decreased by about 1% ISO after 5 stages of black liquor recycling. The final brightness of kraft pulps in series II was lower than that in series I because of the lower pretreatment sulfidity. This confirmed the result obtained from an early study [19].



Series III

The purpose of performing the cooks in Series I and Series II was to study the effect of sulfidity during the black liquor recycling. However, from Series I it seemed that the final pH of the black liquor after the pretreatment influenced the extractive content and bleachability of the kraft pulp to a large extent. It is hard to evaluate whether the drop in the final brightness of the kraft pulps was mainly due to the black liquor recycling or to the drop in the final pH of the pretreatment black liquor. In this series, the effect of the final pH was eliminated. Softwood chips were used and the sulfidity of the pretreatment was kept at 60%. However, the starting active alkali charge of the black liquor was adjusted accordingly so that the final pH of the black liquor was around 12. The properties of the black liquor and kraft pulps after each stage are shown in Figure 4-6 and 4-7.

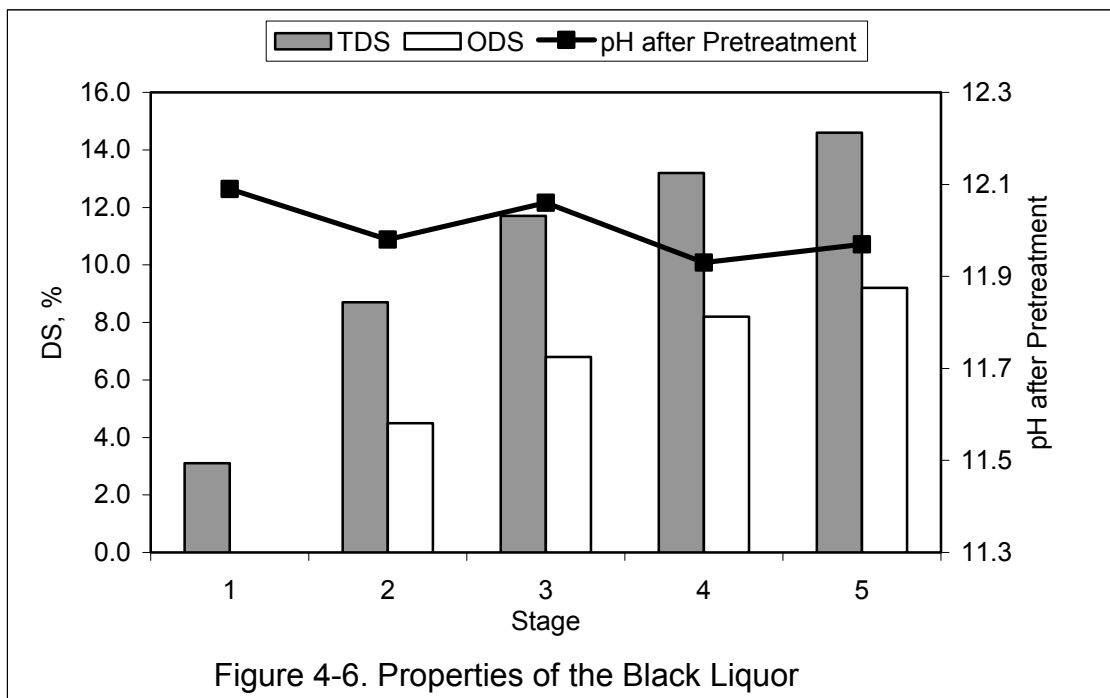
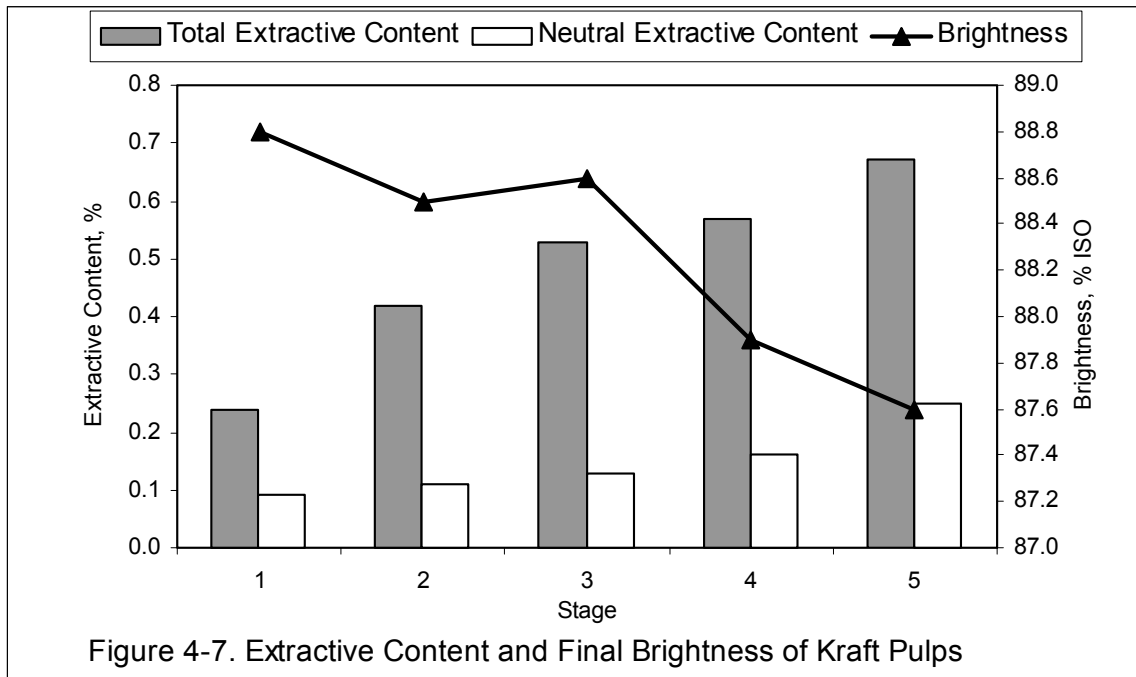


Figure 4-6. Properties of the Black Liquor

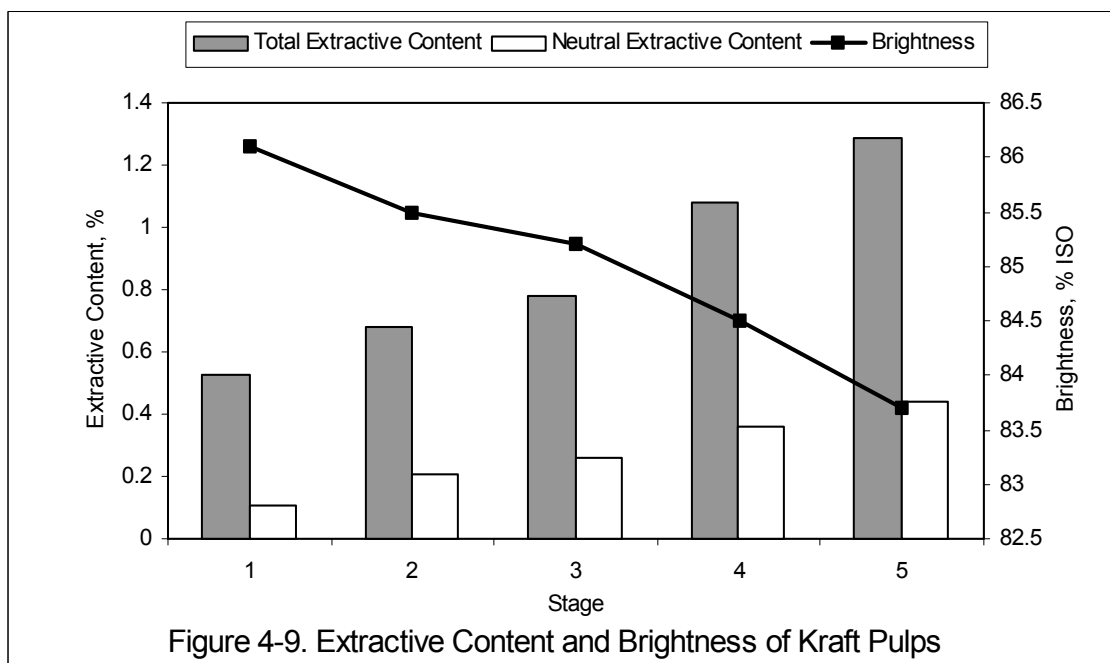
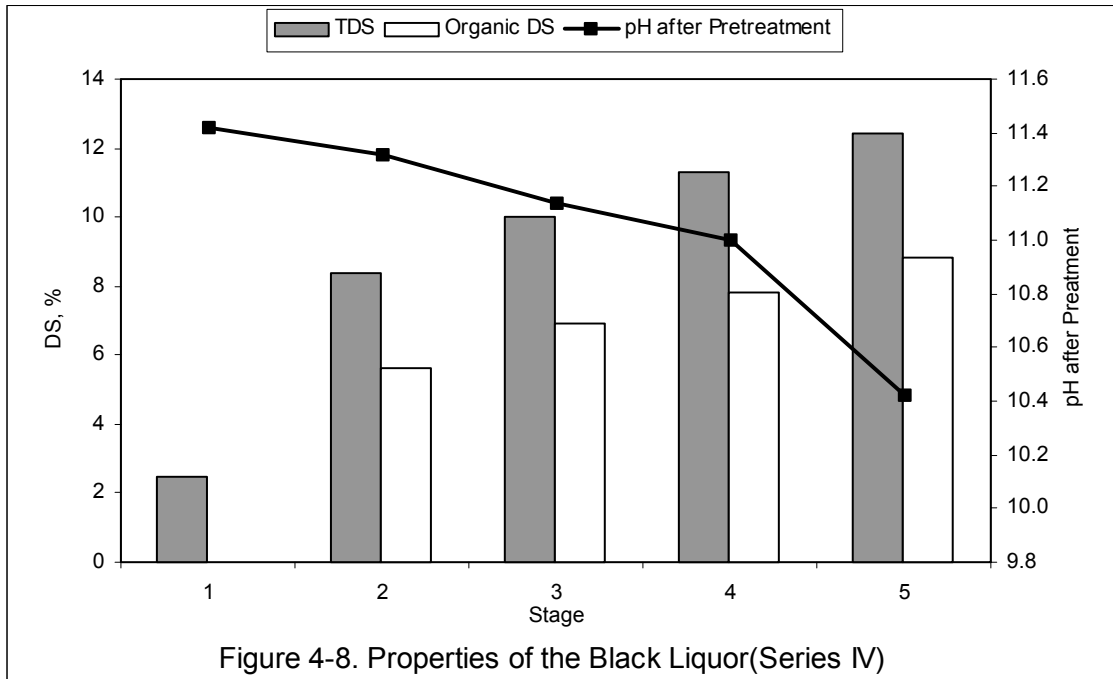


Due to the accumulation of organics in the black liquor, after 5 stages of the black liquor recycling, the total extractive content and neutral extractive content of the kraft pulps were both increased by 2 times, which was much less than in series I. The final brightness of the kraft pulp in the 5th stage was about 1.2% ISO lower than that in the 1st stage. In series I, the difference was about 2%. Therefore, to avoid the further buildup of extractives in pulps, extra alkali should be added to the pretreatment stage after each stage of black liquor recycling to keep the final pH of the black liquor high. White liquor profiling is an efficient way to increase the pH value of the pretreatment liquor and prevent the precipitation of extractives [19].

Series IV

From series I and series III it is easy to understand that if the active alkali charge in the pretreatment stage is lowered, it is easy for the extractives to build up on the surface of the pulps. In this series, softwood chips were used. In the pretreatment, the sulfidity was 60% and the initial active alkali charge was

decreased to 7.5%. The properties of the black liquor and kraft pulps are shown in Figure 4-8 and 4-9, respectively.

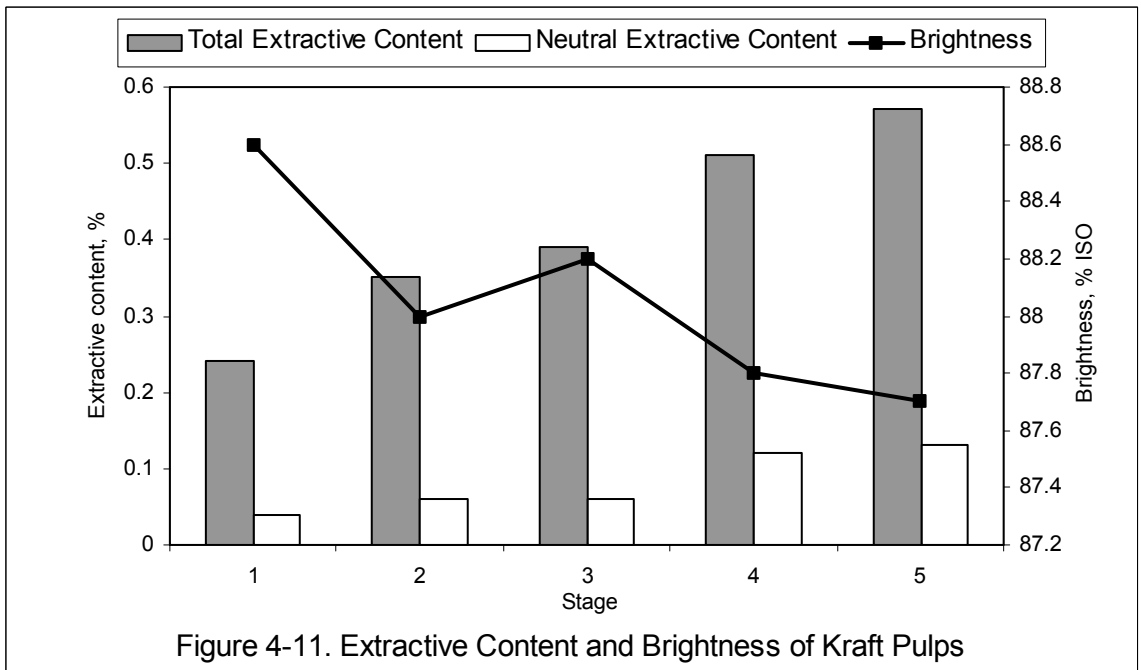
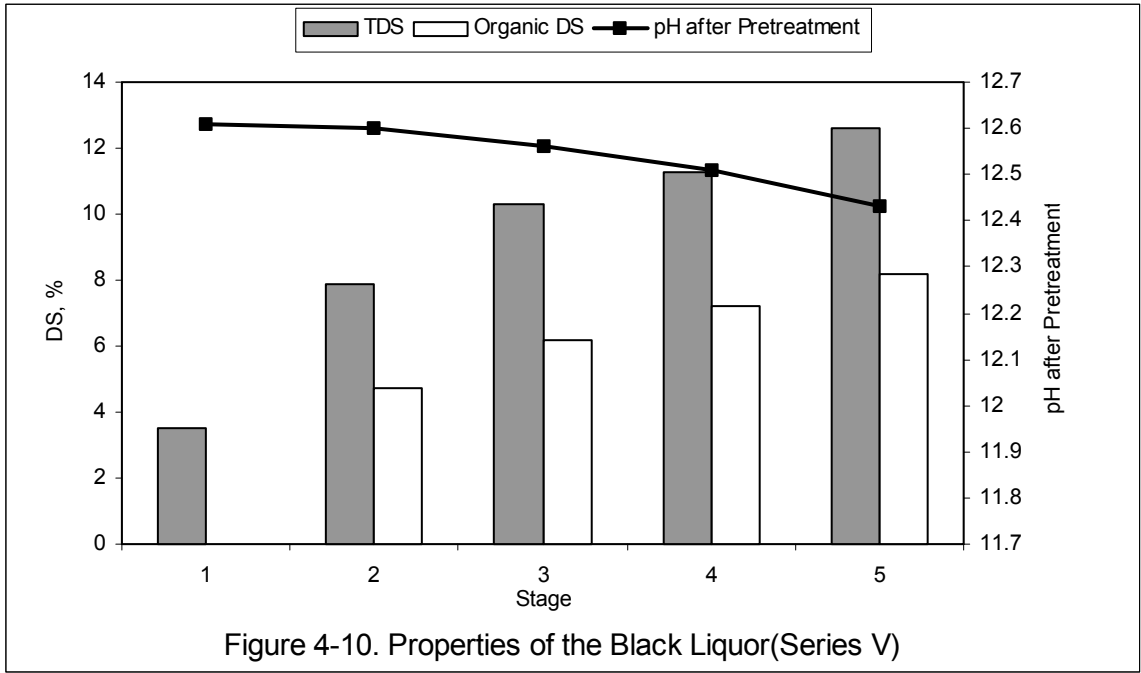


The final pH of the pretreatment black liquor was about 1.0 pH unit lower than that in series I. After 5 stages of black liquor recycling, the final pH of the pretreatment black liquor decreased by around 1.0. Therefore, during the black liquor recycling, it was easier for the extractives to precipitate. The total extractive content and neutral extractive content were higher than that in the corresponding stages in series I. After 5 stages of the black liquor recycling, the total extractive content and neutral extractive content was increased by 2 and 3 times. The final brightness of the kraft pulps was decreased by 2.4% ISO. Obviously, the lower final bleachability of the pulps in this series than in Series I was also due to the lower active alkali charge in the pretreatment. This was confirmed by an early study [19].

Series V

The previous series were all done at a pretreatment temperature of 160°C. At a high pretreatment temperature, the pH of the black liquor dropped drastically at the end of the pretreatment. This may cause the precipitation of lignin fragments and extractives during the pretreatment [8]. The high temperature pretreatment would have an adverse effect on the bleachability of kraft pulps during the black liquor recycling. In this series, the maximum temperature in the pretreatment stage was kept at 130°C. Softwood chips were used. The AA charge was 11% and the sulfidity was 60% at the beginning of the pretreatment. The properties of the black liquor and kraft pulps are shown in Figure 4-10 and 4-11, respectively.

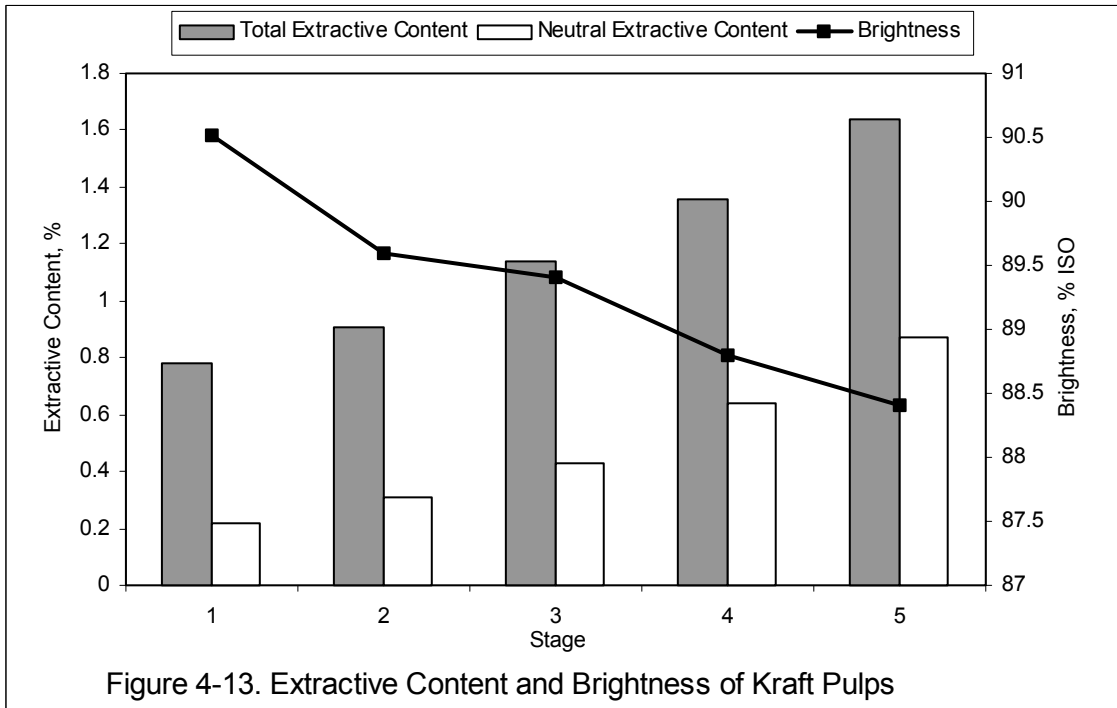
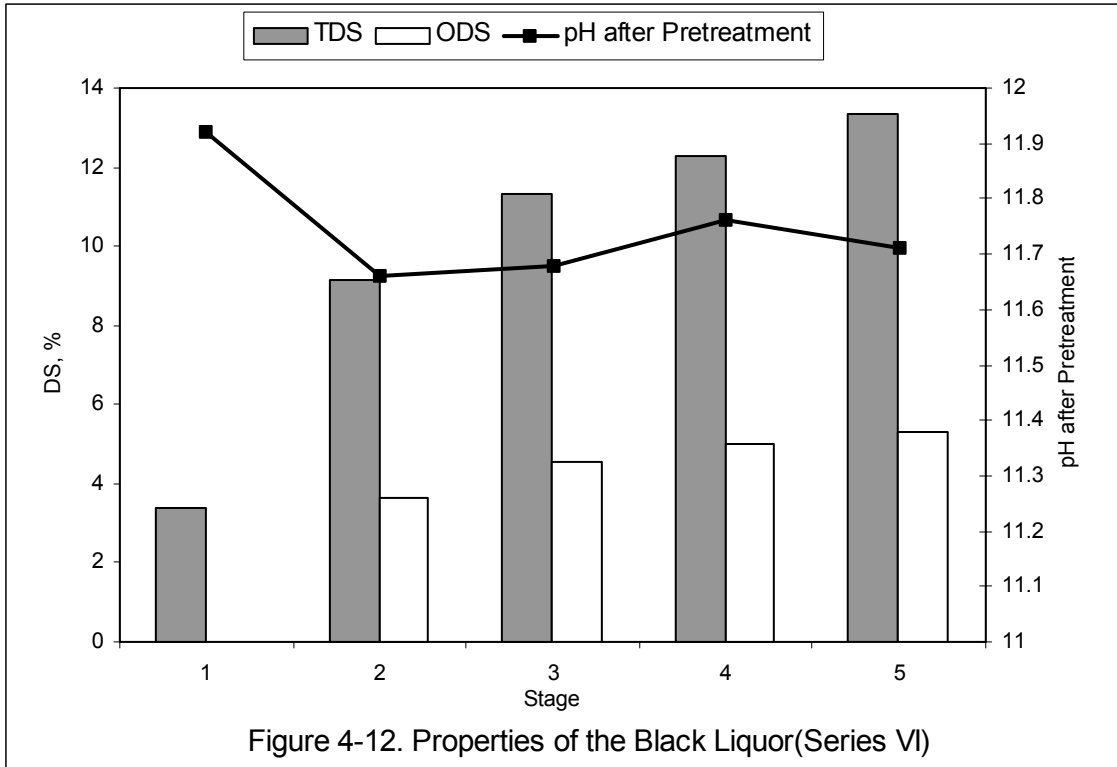
After the low temperature pretreatment, the final pH of the pretreatment black liquor in each stage was at least 0.5 higher than that in the corresponding stage in the high temperature pretreatment cases (Series I). The extractive content of the kraft pulps, especially the neutral extractive content, was much lower than that in the high temperature pretreatment cases. Due to the slow rate of the extractive buildup, the bleachability of the kraft pulp after 5 stages of the black liquor recycling was decreased by less than 1% ISO.



Series VI

As a comparison, the precipitation of extractives of hardwood chips during the black liquor recycling was also studied. Usually the neutral extractive content in hardwoods is higher than that in softwoods. The fatty acid and resin acid content in hardwoods is much lower than that in softwoods. The removal efficiency of neutral compounds in hardwood by the micelle formation mechanism during the kraft pulping is expected to be low [20]. Therefore, during the black liquor recycling, more and more neutral compounds accumulate in the black liquor. They tend to stay with the pulps and finally affect the pulp properties. On the other hand, the kappa number of hardwood kraft pulps is usually much lower than that of the softwood kraft pulps. The charge of bleaching chemicals is generally based on the kappa number of the pulps. Therefore, the extractive content per kappa number for hardwood kraft pulps is much higher than that of the softwood kraft pulps. The black liquor recycling thus will have more pronounced influence on the bleachability of hardwood kraft pulps than on that of softwood kraft pulps.

In this series, hardwood chips were used. The active alkali charge was 11% and the sulfidity was 60% at the beginning of the pretreatment. The properties of the pretreatment black liquors and the hardwood kraft pulps are shown in Figure 4-12 and 4-13.



Due to the higher acidity of oak chips[21], even with the same alkali charge and sulfidity, the final pH of the pretreatment black liquor was a little lower than the corresponding softwood cases. The extractive content of hardwood kraft pulps, especially the neutral extractive content, was much higher than that of softwood pulps. After 5 stages of black liquor recycling, the total extractive content and neutral extractive content was increased by one and three times, respectively. The final brightness of the hardwood kraft pulps was decreased by 2.2% ISO after 5 stages of the black liquor recycling.

Conclusion

In a batch extended delignification process, extractives accumulated in the pulps during the black liquor recycling, which affected the bleachability of pulps. The amount of extractives precipitating onto the pulps depended on the final pH of the pretreatment black liquor. In different series of black liquor recycling, the effects of final pH, sulfidity, sulfidity excluding final pH, alkalinity, pretreatment temperature and wood species were studied. The influence of sulfidity, alkali charge, pretreatment temperature and wood species was summarized as following:

- With a lower sulfidity in the pretreatment, the final pH of the black liquor was higher. A lower amount of extractives precipitated on the fiber surface and the final brightness drop of the pulp was smaller than with a higher sulfidity in the pretreatment. The overall final brightness of the pulps with a lower sulfidity pretreatment was lower than those with a higher sulfidity pretreatment.
- With a lower alkali charge in the pretreatment, the final pH of the black liquor was lower. A larger amount of extractives precipitated onto the fiber surface and the final brightness drop of the pulp was higher than with a higher alkali charge in the pretreatment. The overall final brightness of pulps with a lower alkali charged pretreatment was lower.
- With a lower pretreatment temperature, the final pH of the black liquor was higher. Fewer extractives precipitated onto the fibers and the final brightness

drop of the pulp was smaller than with a higher pretreatment temperature. The overall final brightness of the pulps with a higher pretreatment temperature was comparable to that with a lower pretreatment temperature.

- For the hardwood, a large amount of extractives precipitated on fibers and the extractive content, especially the neutral extractive content of the hardwood kraft pulps was high. During the black liquor recycling, the final brightness drop of hardwood kraft pulps was larger than that of the softwood kraft pulps.

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CHAPTER V

Influence of Pretreatment with Gas-off on the Bleachability and Extractive Content of Extended Delignified Softwood Kraft Pulps

Abstract

The objective of this study is to investigate the impact of pretreatments on the extractive content of pulps. Due to the involvement of various stages of pretreatments, post-treatments and reusing of black liquors during these treatments in batch extended delignification processes, it is very possible that the unsaponifiable extractive compounds accumulate on the fiber surface and affect the bleachability of extended delignified pulps. During the pretreatment stage, if a certain amount of vapor is released (gas-off process), some volatile neutral compounds may be removed with the vapor. A simplified extended delignification pulping process, with only one pretreatment stage and no post-treatment, was used in this study to determine the effect of pretreatment conditions on the bleachability and extractive content of the loblolly pine pulps. White liquors were used in the pretreatment and the gas-off process was included. Using the gas-off process significantly lowered the extractive content, especially the neutral extractive content of pulps. More than 10% of the total neutral wood extractive compounds could be removed from the system during the gas-off. Not only were some of the extractive compounds removed during the gas-off process, but also the distribution of extractive compounds in the cooking system affected the bleachability of pulps. The operating conditions of the gas-off process, such as gas-off temperature and time, as well as the pretreatment alkalinity and sulfidity affected the extractive distribution and extractive content of pulps, and subsequently affected the bleachability. Low gas-off temperature, high sulfidity and high alkalinity in the pretreatments were found to enhance the bleachability of pulps.

Keyword:

Alkalinity, bleachability, extended delignification, extractive content, gas-off, kraft pulping, pretreatment, softwood, sulfidity

Introduction

Due to the increasing environment pressure, it is necessary for pulp and paper industry to develop new methods to reduce the amount of organochlorine in the effluent coming out of bleaching plants. As a result, many new technologies aimed at lowering the lignin content or enhancing the bleachability of the pulp entering the bleaching plant have been developed. Lowering the Kappa number of the pulp by modifying the pulping process has lead to a decrease in chemical usage in bleaching and decrease in AOX discharged from the bleaching plant.

Besides kappa number, the extractives in kraft pulps play an important role in determining the bleachability of pulps. The extractive in wood can be roughly categorized as saponifiables and unsaponifiables. Most of the saponifiables are dissolved in the kraft pulping liquor. However, almost all of the unsaponifiable substances remain in the pulp, increasing the unsaponifiable extractive content of the pulp to more than twice that of the original wood [1]. These unsaponifiable extractives are non-polar, hydrophobic compounds [2]. At the end stage of cooking, when the alkali concentration of the liquor is rather low, the unsaponifiables may re-precipitate on the fiber and the fiber surface is covered with a high amount of extractives [3]. These extractives may affect the bleachability either by reacting with the bleach agents [4, 5, 6, 7, 8] or by lowering the permeability of pulps to bleaching agents. Experiments showed that the bleachability of pulps after organic solvent extraction was much higher than that of the pulps before extraction [9]. Pulps produced from wood with high extractive content have lower bleachability than that from lower extractive content wood species [10,11]. Efforts to lower the extractive content of pulps also resulted in enhancing the bleachability of pulps [12, 13].

The batch extended delignification processes involve various stages of pretreatment and post treatment. During these treatments, the chips are treated with black liquors of different temperature and alkali concentration. The liquors were accumulated from different stages of the cook and reused [14]. In the extended delignification processes, due to the black liquor pretreatment and recycling, more unsaponifiable extractives might accumulate in the black liquor and precipitate on the fiber surface than in the conventional kraft pulping when the alkali concentration is low [9]. This may make the extended delignified kraft pulps harder to bleach than conventional kraft pulps. Previous work has shown that hardwood pulps cooked using the RDH (Rapid Displacement Heating) process were harder to bleach when compared with Kraft-O₂ pulps [15].

From the mill experience, the gas-off process is an effective way to control extractive and enhance the bleachability of RDH pulps[16]. Therefore, the objective of this study is to lower the extractive content, especially those unsaponifiable extractive compounds in the extended delignified pulps by including a gas-off process in the pretreatment. Because there are more operating variables in extended delignification processes than in the conventional kraft process, a simplified extended delignification process was used in this study in order to narrow down the operating variables. This simplified process included only one pretreatment stage and no post treatments.

Experimental

Raw material

A 30-year old loblolly pine tree grown in Raleigh, North Carolina, USA, was used in this study. The wood logs were debarked and then chipped in a laboratory scale chipper. The chips with around 50% moisture content (wet basis) were screened in a laboratory scale screen. The accepts between 1" and 5/8" slots of the screen were used. The chips were kept fresh in the refrigerator at 4°C to prevent extractive loss. The extractive content of the wood was determined by the methods described later and was found to be the following:

Extractive content: 2.47%

Neutral extractive content: 0.17%

Cooking Conditions

The simplified extended delignification cooks were done by using two 7L M&K digester vessels. One of the digester vessels was used for pulping and the other was used as a white liquor accumulator. 1000g OD chips were used in each cook.

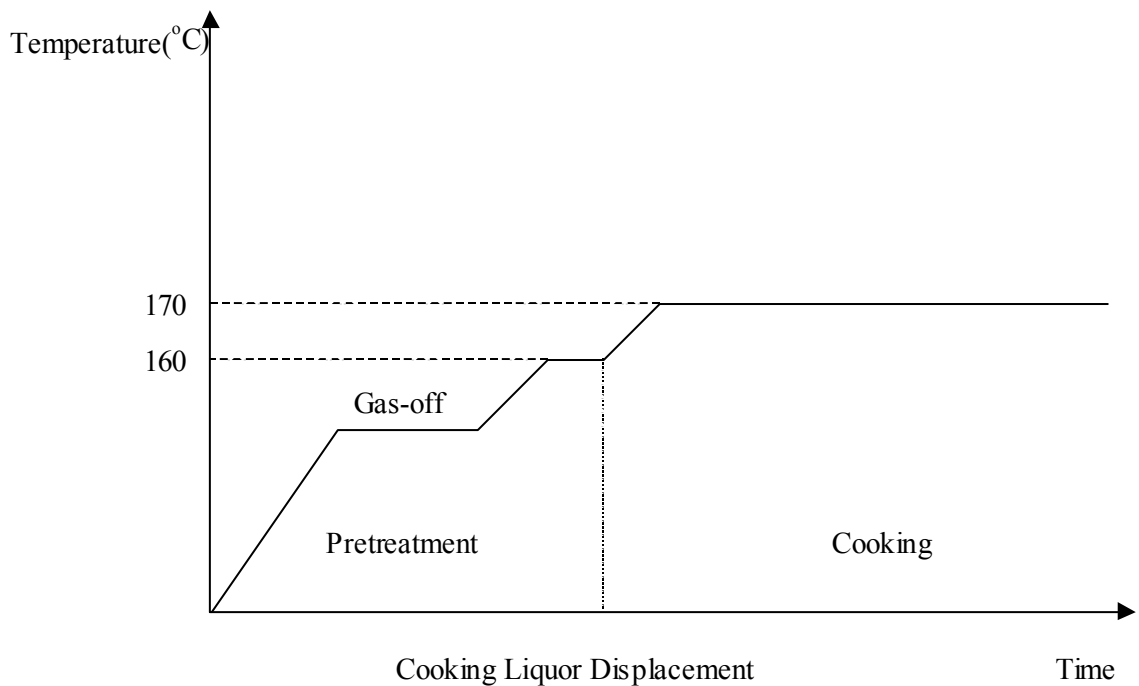


Figure 5-1. Temperature Profile

The temperature vs. time profile used in this procedure is shown in Figure 5-1. The chips were at first pretreated with white liquor containing a certain amount of NaOH and Na₂S. The system was heated to a target temperature (variables) at the rate of 100°C/hr. At that temperature, the top valve of the digester vessel was opened for a given length of time (20 mins unless otherwise

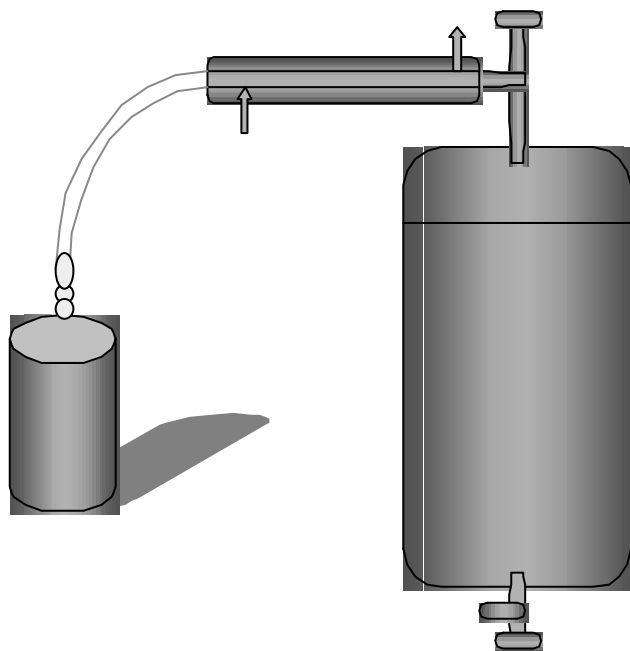


Figure 5-2. Scheme of Gas-off Process

specified) and some vapor was released, which is referred to as the gas-off process. The released vapor was condensed through a condenser and the condensate was collected (shown in Figure 5-2.). The releasing rate was about 12-15 mls condensate per minute. Then the top valve was closed. The system was heated to 160°C at the rate of 100°C/hr and kept for 10 minutes before white liquor displacement. The 2.5 liters of cooking white liquor was preheated to 160°C in the accumulator tank. At the end of the pretreatment stage, the cooking white liquor was transferred to the bottom of the cooking digester to displace 2.5 liters of the pretreatment liquor. After the displacement, the cooking system was heated to 170°C at the rate of 100°C/hr and kept at 170°C for desired H-factor. At the end of the cook, the black liquor was drained. The pulps were thoroughly washed, screened, centrifuged to approximately 30% consistency and fluffed. The cooking conditions are described in Table 5-1.

Table 5-1. Process Conditions for Pretreatment and Cooking

	Pretreatment	Cooking
Active Alkali Charge, as Na ₂ O	0 – 20 g/L	21% Based on OD Chips
Sulfidity	20 – 80%	25%
Liquor Volume	4.5 L	2.5 L Cooking WL
Temperature Increasing Rate	100°C/hr	100°C/hr
Gas-off Time	20 min	N/A
Max. Temperature	160°C	170°C
Time at Max. Temperature	10 min	To H-Factor

Bleaching Conditions

Bleaching was conducted in high density polyethylene (HDPE) bags by mixing the pulp and chemicals together. These bags were sealed and put into a water bath set at 70°C. The bleaching sequence D(E+P)D was used. The detailed operating conditions used during bleaching are listed in Table 5-2.

Table 5-2. Process Conditions for Bleaching.

Stage	Time(hrs)	Temp(°C)	Consistency	Chemical Charge (Based on OD Pulp)	Final pH
D ₁	1	70	10%	K.F. = 0.27	
E + P	1	70	10%	NaOH = 1.5% H ₂ O ₂ = 0.5%	10.3 – 10.9
D ₂	3	70	10%	ClO ₂ = 1.0 %	3.5 – 4.0

Extraction and Fractionation

Samples of wood chips and pulps were dried overnight in a vacuum oven at 45°C. The wood meals were prepared by grinding the wood chip in a Willey mill and sieving through a 40 mesh screen. 20 grams of wood meal (OD basis) or 15 grams of pulp (OD basis) were extracted for at least 10 hrs in a soxhlet

with acetone and then with 95% ethanol. The extracted solutions were combined and the solvents were removed by using a rotavapor at 45°C.

The extracts were hydrolyzed in a flask at 70°C for 4 hrs with 80 ml 0.5N KOH/95% ethanol solution. Then the solution was diluted with 80ml water and the pH of the solution was adjusted to 13.2 ± 0.2 with KOH. The solution was extracted with hexane. The extractive was labeled as the neutral fraction. Then the water phase was acidified to pH around 2.5 by adding 1N HCl and then extracted with chloroform. The extractive was labeled as the saponifiable fraction. The sum of the neutral fraction and the saponifiable fraction was the total extractive content of the sample.

The pH values of black liquor and condensate samples were first adjusted to 13.2 ± 0.2 by adding KOH. Then the samples (full amount of condensate or 100g black liquor) were hydrolyzed at 70°C for 2 hrs. The solution was extracted in a separatory funnel with hexane three times, each with 50ml of hexane. The extractive was labeled as the neutral fraction. Then the water phase of the condensate was acidified to pH 2.5 by adding 4N HCl. The acidified solution was then extracted in a separatory funnel with chloroform three times, each with 50ml of chloroform. The extractive was labeled as the saponifiable fraction. The sum of the neutral fraction and the saponifiable fraction was the total extractive content of the condensate.

The extractive content of the pulp was based on OD pulp. The extractive content of chips, black liquors and condensates were based on OD chip.

Repeatability of the Extraction and Bleaching Processes

The difference in the bleachability and the extractive content was rather small in most cases in this study. In order to evaluate the significance of the extraction and bleaching data, the reproducibility was investigated. Three cases were randomly chosen. In each case, three independent cooks were performed. Two replicates of extraction and bleaching were tested for each cook. The 95% confidence interval was deduced from the 6 replicates of the measurements.

Table 5-3. Repeatability of Extraction and Bleaching Processes with 95% Confident Interval

	After Pretreatment Before Cooking						After Cooking			
	Condensate			Black Liquor		Chips	Pulps			
	pH	TEC (%)	NEC (%)	pH	NEC (%)	NEC (%)	Kappa #	Bright. (ISO%)	TEC (%)	NEC (%)
Case 1	6.29 ±0.11	0.0403 ±0.0018	0.0177± 0.0009	10.51 ±0.19	0.0158± 0.0012	0.085± 0.006	24.0 ±0.4	86.3 ±0.3	0.22 ±0.02	0.12 ±0.01
Case 2	3.72 ±0.08	0.0588± 0.0023	0.0210± 0.0009	4.53 ±0.13	<0.0004	0.166± 0.007	23.2 ±0.4	84.5 ±0.4	0.50 ±0.02	0.24 ±0.01
Case 3	7.18± 0.23	0.0233± 0.0016	0.0151± 0.0007	12.11 ±0.15	0.0192± 0.0011	0.048± 0.005	23.3 ±0.3	86.0 ±0.4	0.24 ±0.01	0.08 ±0.01

Case 1: 20g/L AA as Na₂O, 60% sulfidity in pretreatment, 160°C gas-off

Case 2: 0 g/L AA as Na₂O in pretreatment, 140°C gas-off

Case 3: 20g/L AA as Na₂O, 20% sulfidity in pretreatment, 160°C gas-off

According to the confidence intervals in Table 5-3, most of the extraction data in this study were significantly different from each other. The repeatability of some data, such as the final brightness and neutral extractive contents of pulps and treated chips were satisfactory. The difference in the bleachability of the same pulp was in the range about ±0.3% ISO. Some of the bleaching results were marginally different. The extractive content of the condensate had a fair repeatability. The repeatability of the neutral extractive content of the black liquor was rather poor. Most of the data from the black liquor extraction were not significantly different. Experiments found that the properties of the black liquors, such as the residual alkali and the dissolved solid content, affected the extractability of the extractives in the black liquors.

Results and Discussion

Effect of Gas-off Temperature

The gas-off process caused some of the extractives to be removed from the pulping system, resulting in a improved bleachability and a decreased

extractive content of kraft pulps. The bleachability and the extractive content of pulps are shown in Table 5-4 for different gas-off temperatures. In all gas-off cases, the pulp bleachability was increased by 0.5 – 1.0% ISO and the extractive content of the pulps was decreased by 0.1 – 0.2%. The neutral extractive content of the pulps also decreased by 0.1 – 0.2%. With a low temperature gas-off (120 – 140°C), the brightness after bleaching was increased around 1% ISO. The extractive content was decreased by 0.1%. With a high temperature (160°C) gas-off, the brightness after bleaching was increased around 0.5% ISO. The extractive content was decreased by 0.2%. If gas-off was performed during the whole heating process (100°C–160°C), more extractives could be removed because of the longer gas-off time. The resulted pulp had a low total extractive content and neutral extractive content and good bleachability.

Table 5-4. Effect of Gas-off Temperature on Extractive Content and Bleachability of Pulps
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

Gas-off Temp(°C)	Gas-off Time(min)	Kappa Number	Final Bright. (% ISO)	TEC (%)	NEC (%)
None	0	24.1	86.0	0.44	0.21
120	20	23.3	86.9	0.32	0.11
130	20	23.6	87.0	0.32	0.07
140	20	23.2	87.1	0.35	0.09
160	20	24.3	86.5	0.23	0.12
100 - 160	40	23.8	86.9	0.24	0.06

TEC: total extractive content

NEC: neutral extractive content

Compared to pulps that were pretreated with gas-off at a low temperature, the pulp pretreated with gas-off at 160°C had lower extractive content, but lower bleachability. The total extractive content is not a good indication of the bleachability of the pulp. The pulp extractive is a mixture of hundred of

compounds. Not all of them necessarily influence the pulp bleachability. Extractives can be roughly divided into saponifiables and unsaponifiables. Most of the unsaponifiable materials in the wood will be carried through with the pulps and these extractives are also less polar and more troublesome [1]. In this study, the extractives were divided into two fractions, the neutral part and the saponifiable part. Most of neutral extractives were unsaponifiables [17]. From the neutral extractive content of pulps it can be seen that when the gas-off was performed at low temperature, the higher bleachability of the pulps was due to their relatively lower neutral extractive content.

The extractive content of the gas-off condensate was also studied. The condensate was a strong-smelling, cloudy water/organics mixture with the color ranging from clear light yellowish to milky white. As Table 5-5 shows, up to 2% of the total extractives and up to around 10% of the total neutral compounds were found in the condensate. When the gas-off temperature increased, more extractives came out with the condensate. More neutral extractives also came out. At a high gas-off temperature, the percentage of neutral fraction in the condensate extractives decreased, which resulted in the lower pH value of the condensate.

Table 5-5. Effect of Gas-off Temperature on Extractive Content of Gas-off Condensate
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

Gas-off Temp(°C)	Gas-off Time (mins)	pH of Condensate	TEC (%)	NEC (%)	NF (%)
120	20	8.75	0.0184	0.0084	46
130	20	6.89	0.0252	0.0146	58
140	20	6.45	0.0356	0.0162	46
160	20	6.27	0.0408	0.0177	43
100-160	40	7.11	0.0361	0.0184	51

TEC: total extractive content

NEC: neutral extractive content

NF: Neutral Fraction of Condensate Extractive (%)

Apparently, a contradiction appears here. At a higher gas-off temperature, more extractives and more neutral extractives were removed from the system with the condensate, which should have resulted in lower neutral extractive content and higher bleachability of the pulp. Why then does the bleachability favor the low gas-off temperature? Three possible reasons were proposed to account for the relatively high bleachability with gas-off at low temperatures. First, the residual lignin in the pulps may be easier to be removed at lower pretreatment temperatures. Second, some new extractives, which affect the bleachability, may be generated at high pretreatment temperatures. Finally, after a high temperature pretreatment, the alkali concentration of the pretreatment liquor dropped dramatically, which may change the distribution of the extractives and in the end affect the bleachability of the pulp. Detailed studies were carried out to verify these reasons.

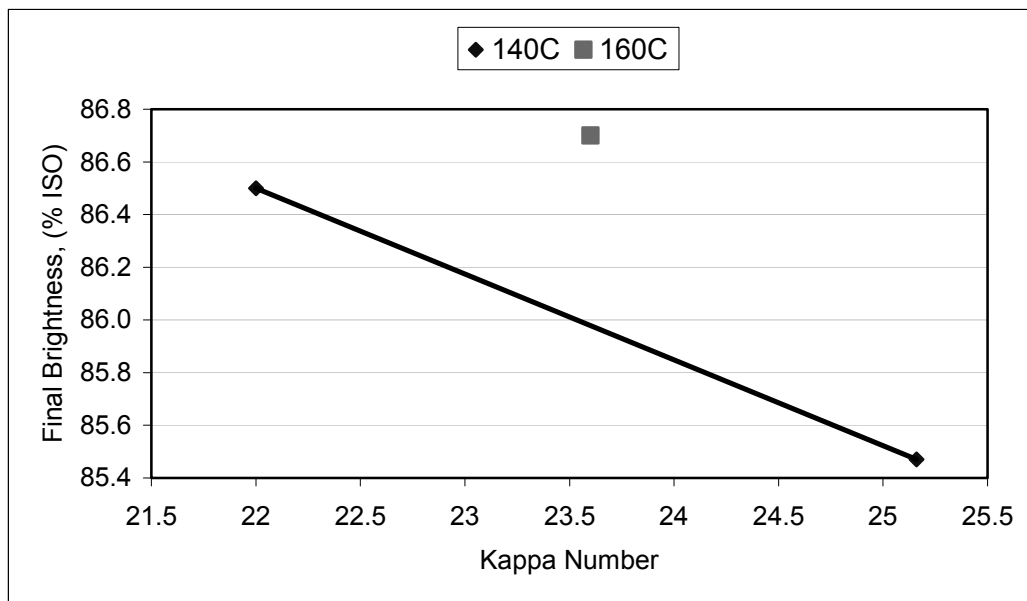


Figure 5-3. Final Brightness Vs. Pretreatment Temperature (No Gas-off)
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment without gas-off)

Figure 5-3 shows the brightness of pulps after bleaching vs. pretreatment temperature. In this study, in order to exclude the effects of the gas-off and the black liquor displacement on the extractive distribution in the system, only half the amount of the chips and liquors were used so that all the chips, pretreatment liquor and cooking liquor could be put into the digester. No black liquor was displaced out of the digester before the cook finished. No gas-off was performed. The temperature vs. time profile used in this procedure was kept the same as the gas-off processes. The results indicated that a higher pretreatment temperature resulted in a higher bleachability of the pulp. Therefore, higher gas-off temperature should have resulted in higher bleachability, which excluded the residual lignin possibility.

The dispersion of the neutral compounds in the cooking liquor was due to the micellar solubilization by fatty acids and resin acids in the form of sodium soap [18, 19]. These soaps serve as the surface active components to form micellar particles. The neutral compounds are enclosed by the hydrophobic tails turning to the inside of the micelles while the hydrophilic heads turn outside towards the solution. The micelles are negative charged. These micelles make the neutral compounds suspend stable in the alkaline cooking liquor. The solubility of the micelles depends on the solubility of the soap [19] and the pH of the liquor. When the pH is high, the dissociation of the phenolic groups on the fiber surface increases the fiber surface charge. The electrostatic repelling force between the fiber surface and the negatively charged micelles prevents the precipitation of the micelles on the fiber surface.

The pH value of the pretreatment liquor and extractive distribution before and after the cook are shown in Table 5-6. During the pretreatment, at a higher gas-off temperature, more alkali was consumed. There was a larger drop in the pH of the system. Some of the neutral extractives suspended in the pretreatment black liquor re-precipitated onto the fiber surface. Even through the gas-off process could remove some of the neutral extractives, after the cooking liquor displacement, less neutral extractive compounds came out with the pretreatment

liquor. Therefore, there was still higher concentration of neutral extractives left in the digester, which resulted in a higher neutral extractive content in the pulp. The higher neutral extractive content in the pulp resulted in lower bleachability. Therefore, one effective way to increase bleachability is to maintain high alkali concentration during the pretreatment stage right before the cooking stage so that more extractives can be removed by the cooking liquor displacement. In another study, Kumar found that in a RDH cooking with white liquor profiling, when all the split white liquor was used in the hot fill stage (the pretreatment stage right before the cooking), the maximum bleachability was achieved [20]. It was suggested that the enhanced bleachability of the pulp could be partly due to more efficient removal of dissolved organics.

Table 5-6. Extractive Distribution before and after the Cooking
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

Gas-off Temp(°C)	After Pretreatment before Cooking			After Cooking		
	NEC in Chips(%)	pH of Black Liquor	NEC in BL(%)	NEC in Pulp(%)	pH of Black Liquor	NEC in BL(%)
140	0.069	11.43	0.0177	0.094	13.27	0.073
160	0.084	10.52	0.0160	0.122	13.19	0.067

Table 5-7 shows the neutral extractive balance before and after the pretreatment without gas-off. With a high temperature pretreatment, neutral extractive content increased by 7%. The increase indicated that when pretreated at a high temperature and a high sulfidity (described later), some organics might react with the sulfide or polysulfide in the liquor to generate some new neutral compounds. These newly generated neutral compounds might affect the bleachability of the pulp. The structural change of the extractive compounds after a high temperature pretreatment needs to be studied in more detail. However,

according to Figure 5-3, the adverse effect of the new generated neutral extractive seemed not as large as the positive effect of the modification of the residual lignin when treated at a high temperature and sulfidity. The effect of the sulfidity will be studied later in more detail.

Table 5-7. Neutral Extractive Balance after Pretreatment (without Gas-off)

Temp(°C)	% S	After Pretreatment					
		NEC in Chip		NEC in Black Liquor		Total	Ratio
		%	Weight(g)	%	Weight	NEC(g)	
160	80	0.089	0.344	0.0159	0.380	0.724	1.07
140	80	0.070	0.273	0.0168	0.401	0.674	1.00

Effect of Pretreatment Alkalinity

The effect of the alkali concentration in the pretreatment can be more clearly seen in the following study. The active alkali charges in the pretreatment varied from 0 g/L to 20g/L as Na₂O. Table 5-8 shows the bleachability and the extractive content of the pulps. When the active alkali charge in the pretreatment increased, the bleachability of the pulps increased. At the same time, the extractive content and the neutral extractive content in the pulps decreased. When pretreated with 0g/L active alkali charge, the bleachability of the pulp was even lower than that without gas-off.

The compositions of the condensate, pretreatment liquors and chips after the pretreatment are shown in Table 5-9. The lower the alkalinity in the pretreatment, the greater the amount of extractive that came out during the gas-off process. The amount of neutral extractive compounds that came out was also higher. Obviously, because of the low active alkali charge in the pretreatment, a lot of acidic compounds came out with the steam, which resulted in a low pH of the condensate. However, because of the low active alkali charge, the pH value

of the black liquor was low. More extractive will stay in the chips under the low alkali conditions instead of suspending stably in the pretreatment liquor. After the cooking liquor transferring, less neutral compounds would be transferred out of the system. When the active alkali charge was 0, almost all the neutral compounds stayed with the chips and were carried into the cooking stage, which resulted in a much higher neutral extractive content in the pulp.

Table 5-8. Effect of Pretreatment Alkalinity on Extractive Content and Bleachability of Pulps (60% sulfidity, white liquor pretreatment with gas-off at 140°C)

AA in Pretreat. (g/L as Na ₂ O)	Gas-off Time (mins)	Kappa Number	Brightness (% ISO)	TEC (%)	NEC (%)
0	20	22.8	84.9	0.52	0.22
10	20	23.7	85.3	0.44	0.17
20	20	23.2	87.1	0.35	0.09
20	None	24.1	86.0	0.44	0.21

Table 5-9. Effect of Alkalinity in Pretreatment on Neutral Extractive Content (60% sulfidity, white liquor pretreatment with gas-off at 140°C)

AA in Pretreat. (g/L)	Gas-off Time (mins)	After Pretreatment before Cooking						
		Condensate				Black Liquor		Chips
		pH	TEC (%)	NEC (%)	NF (%)	pH	NEC (%)	NEC (%)
0	20	3.70	0.0585	0.0203	35	4.55	<0.0005	0.166
10	20	5.69	0.0425	0.0166	39	9.94	0.0053	0.127
20	20	6.43	0.0356	0.0162	46	11.43	0.0177	0.069
20	None	None	None	None	None	11.47	0.0188	0.076

Effect of Pretreatment Sulfidity

The sulfidity in the pretreatment also affected the bleachability and the extractive content of pulps. In the previous section, it was mentioned that when

the gas-off is done at a high temperature, some new neutral compounds were generated and they might lower the bleachability of the pulps. It was also found that at different temperatures, the sulfidity had different effects on the extractive content of pulps. Therefore, as listed in Table 5-10, two different gas-off temperatures were chosen to see the influence of sulfidity at high and low temperatures. At a low temperature, the sulfidity had little effect on the total neutral extractive content in the system. At a high temperature, after a high sulfidity pretreatment, the total neutral extractive content in the whole system increased by 9%. Some new neutral compounds were generated, possibly by the reaction of neutral compounds with sulfur compounds, only at high temperatures and high sulfidity.

Table 5-10. Neutral Extractive Balance after Pretreatment (without Gas-off)

Temp(°C)	% S	After Pretreatment					
		NEC in Chip		NEC in Black Liquor		Total	Ratio
		%	Weight(g)	%	Weight	NEC(g)	
160	80	0.089	0.344	0.0159	0.380	0.724	1.09
160	20	0.053	0.190	0.0196	0.474	0.664	1.00
140	80	0.070	0.273	0.0168	0.401	0.674	1.02
140	20	0.047	0.181	0.0204	0.488	0.669	1.01

In the following studies, the initial active alkali charges in the pretreatment were kept the same but the sulfidity was varied. As shown in Table 5-11, when pretreated with a higher sulfidity, pulps resulted in a higher bleachability but a higher total extractive content and neutral extractive content. At a low sulfidity, the gas-off temperature seemed to have little effect on the bleachability and the extractive content of the pulps.

Table 5-11. Effect of the Pretreatment Sulfidity on Bleachability and Extractive Content in Pulps
(20g/L AA as Na₂O, white liquor pretreatment)

Gas-off Temp(°C)	Sulfidity	Kappa Number	Brightness (% ISO)	TEC (%)	NEC (%)
140	60%	23.2	87.0	0.35	0.09
160	60%	24.3	86.5	0.23	0.12
140	20%	23.7	86.0	0.27	0.08
160	20%	23.3	86.1	0.24	0.08

Table 5-12. Effect of Pretreatment Sulfidity on Neutral Extractive Content
(20g/L AA as Na₂O, white liquor pretreatment)

Gas-off Temp (°C)	Sulfidity	After Pretreatment Before Cooking						
		Condensate				Black Liquor		Chips
		pH	TEC(%)	NEC(%)	NF(%)	pH	NEC(%)	NEC(%)
140	60%	6.43	0.0356	0.0162	46	11.43	0.0177	0.069
160	60%	6.27	0.0408	0.0177	43	10.52	0.0160	0.084
140	20%	7.53	0.0165	0.0122	68	12.49	0.0204	0.047
160	20%	7.18	0.0236	0.0151	64	12.13	0.0196	0.053

The neutral extractive contents of the condensate, black liquors and chips after pretreatment are listed in Table 5-12. As the sulfidity in the pretreatment liquor increased, the total extractive content and the neutral extractive content in the condensate increased. As the gas-off temperature increased, the total extractive content and the neutral extractive content in the condensate increased. At a low sulfidity, the pH of the pretreatment liquor was higher and fewer acidic compounds came out with the vapor. Therefore, the pH value of the condensate was higher and the percentage of neutral compounds in the condensate extractives was also higher. On the other hand, the lower the sulfidity and the lower the gas-off temperature in the pretreatment, the higher the pH value of the black liquor was. More neutral extractive could suspend in the

black liquor. After cooking liquor displacement, less neutral extractive would stay in the cook, which resulted in lower extractive and neutral extractive contents in the chips and pulps. Interestingly, even though the pulp had higher neutral extractive content after a higher sulfidity pretreatment, the pulp bleachability was higher. The higher bleachability was likely due to the structural modification of the residual lignins after the pretreatment with the high sulfidity liquor. When chips are treated with the high sulfidity liquor, the delignification process is more selective [21]. The residual lignin may be more reactive. The high reactivity of the residual lignin seemed to compensate for the drawback of the high neutral extractive content in the pulps.

Conclusion

It is possible to modify the bleachability and the extractive content of extended delignified softwood kraft pulps by introducing a gas-off process in the pretreatment. The results of the present study can be summarized as follows:

- The gas-off process affected the extractive content and the bleachability of the pulps.
- The extractive content affected the bleachability of the extended delignified pulps. The neutral fraction of the extractives seemed to have larger influence on the bleachability.
- The conditions of the pretreatment in the batch extended delignification process, such as gas-off temperature, sulfidity, alkalinity affected the bleachability of pulps.
- Low gas-off temperatures and high alkalinity in pretreatments lowered the neutral extractive content and resulted in a high bleachability of pulps. High sulfidity in pretreatments increased the neutral extractive content. The high bleachability of pulps may be due to the modification of the residual lignin.

- Higher amount of extractives was removed with a gas-off at high temperatures than at low temperatures and more extractives were removed when pretreated with a low alkali charge than with a high alkali charge.

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CHAPTER VI

Influence of Pretreatments with High Temperature Gas-off on the Bleachability and Extractive Content of Extended Delignified Softwood Kraft Pulps

Abstract

The objective of this study is to investigate the impact of pretreatments with a high temperature gas-off process on extractive content and bleachability of pulps. A simplified extended delignification pulping process, with only one pretreatment stage and no post treatment (except for one stage washing), was used in this study to determine the effect of operating conditions in the pretreatment on the bleachability and the extractive content of the loblolly pine kraft pulps. Both white liquors and black liquors were used in the pretreatment and a high temperature gas-off process was included. Presteaming, white liquor profiling(WLP) and caustic washing were three efficiency methods to enhance the performance of high temperature gas-off processes. For the pretreatments with white liquors, the modified high temperature gas-off processes significantly lowered the extractive content, especially the neutral extractive content of pulps. Presteaming, WLP to the pretreatment liquor after gas-off, WLP to the washing liquor(enhanced washing) were found to lower the extractive content and improve the bleachability of kraft pulps. For the pretreatment with black liquors, the gas-off process had little influence on the extractive content and the bleachability of the pulp. WLP to the pretreatment liquor and WLP to the washing liquor were found to improve the bleachability of the pulps. A kinetic study revealed that more extractives were removed when pretreated with white liquor than with black liquors by the gas-off process. More extractives were removed during the first several minutes of releasing. Therefore, the rate of the extractive removal leveled off.

Keyword:

Black liquor, bleachability, extended delignification, extractive content, gas-off, kraft pulping, presteaming, pretreatment, softwood, washing, white liquor profiling

Introduction

Batch extended delignification processes involve different stages of warm black liquor and hot black liquor pretreatment to save energy and extend delignification [1, 2]. The warm and hot black liquors used in the pretreatment are made up of cooking liquors that are recycled from the previous cook. Due to the multistage black liquor pretreatment and recycling, the unsaponifiable compounds accumulate in the pretreatment black liquors. Thus, there is a greater chance for the unsaponifiable extractives to precipitate onto the fiber surface than in the conventional kraft pulping when the alkali concentration in the liquor is low. This may make the extended delignified kraft pulps harder to bleach than conventional kraft pulps.

It has been demonstrated that the bleachability of softwood pulps, cooked by a batch extended delignification process, was enhanced by implementing a gas-off process in the pretreatment [3]. During the gas-off process, some of the volatile extractive compounds could be removed from the digester, which resulted in a lower extractive content in the pulp. The bleachability of the pulps was then improved. The operating conditions of the gas-off process affected the extractive content and the bleachability of pulps. In our previous study, we found that for the high temperature gas-off process (160°C), when pretreated with white liquors, more than 10% of the neutral extractive compounds in wood chips could be removed [4]. More extractives were removed in a high temperature gas-off than in low temperature gas-off processes. However, because the pH of the pretreatment liquor dropped dramatically during the high temperature gas-off, the extractive distribution between the pretreatment liquor and the chips was affected. More extractive compounds precipitated onto the fiber surface when the alkali concentration was low. The resulting pulps had a higher extractive

content and a lower bleachability than the pulps with a lower temperature gas-off.

In the real world, a batch extended delignification process involves various stages of pretreatment and post-treatment. The temperature of the last pretreatment stage is around 160°C [1]. Even the initial temperature of the last pretreatment after the hot black liquor displacement is too high to perform a low temperature gas-off [5]. Therefore, it is more practical to perform the gas-off at a high temperature while maintaining the high alkali concentration in the pretreatment liquor. White liquor profiling (WLP) helps in maintaining a uniform and high alkaline concentration during the pretreatment [6]. This may make the neutral extractive compounds more stable in the liquor and thus prevent their reprecipitation on the fiber surface [7].

On the other hand, more extractives can be removed when the gas-off is performed at a high temperature. The only drawback of a high temperature gas-off is the faster delignification reaction. More alkali was consumed at a high temperature pretreatment and there was a larger drop in the pH of the system. However, this result was based on one-stage pretreatment. If there are more than one stages of pretreatment, due to the effect of the previous stage of pretreatment, the difference of pH in the last stage of pretreatment may decrease which would make high temperature gas-off more favorable.

Therefore, the objective of this study is to modify the high temperature gas-off process in the pretreatment in an extended delignification kraft pulping. Three methods, presteaming, WLP, caustic washing, were used in this study to lower the extractive content in pulps. Like in our previous study, a simplified extended delignification process was used in this study in order to narrow down the operating variables. Such simplified process included only one pretreatment stage with the alkali concentration similar to that of the hot fill treatment of real RDH cooking and no post treatments, except for one washing stage used in some cases to evaluate the effect of caustic washing. The effects of gas-off, WLP, washing in black liquor pretreatment were also evaluated.

Experimental

Raw material

A 30-year old loblolly pine tree grown in Raleigh, North Carolina, USA, was used in this study. The wood logs were debarked and then chipped in a laboratory scale chipper. The chips with around 50% moisture content (wet basis) were screened. The accepts between 1” and 5/8” slots of the screen were used. The chips were kept fresh in the refrigerator at 4°C to prevent the loss of extractives. The extractive content of the wood was determined following:

Extractive content: 2.47%

Neutral extractive content: 0.17%

The black liquor used in the pretreatment in this study was generated in our lab. The properties of the black liquor were determined as following:

AA: 22g/L as Na₂O

Sulfidity: 52%

DS: 16.97%

pH: 13.18

Cooking Conditions

The simplified batch extended delignification kraft cooks were done by using three 7L M&K digester vessels. One of the digester vessels was used as the digester pulping and the other two were used as black liquor/white liquor accumulators. 1000g oven dry chips were used in each cook. The details of the cooking process are described elsewhere [4]. The target kappa number was 24. The cooking conditions are given in Table 6-1. For some cases, there was a washing stage performed after the cooking stage. At the end of cooking, 5 liters of preheated washing liquor (white liquor only) was transferred to the digester to displace 5 liters of cooking black liquor. The washing liquor was circulated in the digester for 20 mins and drained.

Table 6-1. Process Conditions for Treatments and Cooking

	Pretreatment	Cooking	Washing
Active Alkali Charge as Na ₂ O	20 g/L	21% on OD Chips	8 g/L
Sulfidity	60%	25%	25%
Liquor Volume	4.5 L	2.5 L Cooking WL	5.0 L
Temperature Increasing Rate	100 °C/hr	100 °C/hr	N/A
Preheated Temperature	None	160 °C	70 °C
Max. Temperature	160 °C	170 °C	N/A
Time at Max. Temperature	10 min	To H-factor	N/A
Gas-off Temperature	130°C to 160 °C	N/A	N/A

Table 6-2 shows the processes with two stages of pretreatment. In both pretreatment stages, only white liquors were used. The hot liquor and the cooking liquor were preheated to 160°C before displacement. After the warm liquor pretreatment, the black liquor was drained. The hot pretreatment liquor was transferred to the digester. No displacement was performed when transferring the hot pretreatment liquor to the digester.

Table 6-2. Process Conditions for Two-Stage Pretreatment

	Warm Liquor Pretreatment	Hot Liquor Pretreatment	Cooking
AA Charge as Na ₂ O	16 g/L	20 g/L	21% on OD Chips
Sulfidity	60%	60%	25%
Liquor Volume	4.5 L	4.5 L	2.5 L Cooking WL
Temperature Increasing Rate	100 °C/hr	100 °C/hr	100 °C/hr
Preheated Temperature	None	160 °C	160 °C
Max. Temperature	140 °C	160 °C	170 °C
Time at Max. Temperature	10 min	10 min	To H-Factor
Gas-off Temperature	None	140 °C or 160 °C	N/A

In the cases with white liquor profiling, the liquor containing 3% AA charge (based on OD chips, about 358ml cooking white liquor) was transferred to the pretreatment stage or the washing stage.

Chip Flashing

Chip flashing refers to the gas-off process when there are only chips in the digester. After the pretreatment, all black liquor was transferred to an accumulating tank. The digester with chips and pressurized steam was released to the atmospheric pressure. Then the black liquor was transferred back to the digester and heated to 160°C. In the single-flash case, when the temperature reached 160°C, the cooking white liquor was transferred to the digester to displace some of the pretreatment black liquor and the cooking stage started. In the 3-flash case, when the temperature reached 160°C, the black liquor was transferred out and the chip was flashed repeatedly. The chip was flashed three times before the cooking liquor was transferred to displace some of the pretreatment black liquor.

Bleaching Conditions

Bleaching was conducted in high density polyethylene (HDPE) bags by mixing the pulp and chemicals together. These bags were sealed and put into a water bath set at 70°C. The bleaching sequence D(E+P)D was used. The detailed operating conditions used during bleaching were listed in Table 6-3.

Table 6-3. Process Conditions for Bleaching

Stage	Time (hrs)	Temperature (°C)	Consistency	Chemical Charge	Final pH
D ₁	1	70	10%	K.F. = 0.27	
E + P	1	70	10%	NaOH = 1.5% H ₂ O ₂ = 0.5%	10.3 – 10.9
D ₂	3	70	10%	ClO ₂ = 1.0%	3.5 – 4.0

Extraction and Fractionation

The details for the extraction and fractionation processes were described elsewhere [4].

Results and Discussion

Effect of Chip Flashing

In the previous processes, the gas-off was performed to the system with both the pretreatment liquor and chips. Flashing of chips may be the most straightforward process. If all the liquor was transferred out of the system after pretreatment, and the gas-off was performed on the chips alone, only the extractives staying with the chips would be removed. The extractives in chips are believed to have the final influence on the bleachability of the pulps. Table 6-4 shows the effect of chip flashing on the extractive content and bleachabilities of pulps.

Table 6-4. Influence of Chip Flashing on the Bleachability and Extractive Content of Pulps

	Without Flash	With 1 Flash	With 3 Flash
Brownstock Kappa Number	23.9	25.0	24.7
Final Brightness (ISO, %)	87.9	87.3	88.4
Total Extractive Content (%)	0.30	0.37	0.41
Neutral Extractive Content (%)	0.18	0.19	0.19

After flashing the chips, some of the neutral extractives in the chips can be removed by the flashing process. However, unlike the previous gas-off processes, chip flashing is a short, one-time gas-off. Only the extractives with the pressurized steam left in the digester will be released. After the black liquor had been transferred out of the digester, the temperature in the digester decreased to around 130°C. Under such low gas-off temperature, some volatile substances may condense and stay in the digester. Therefore, the neutral

extractive removal efficiency in chip flashing was not as high as in the previous gas-off processes [8]. Due to the transferring of the black liquor back and forth during the chip flashing, some of the extractive in the black liquor was adsorbed by the fiber surface. The neutral extractive content was not lowered but the total extractive content was increased after chip flashing. The difference in pulp bleachability was marginal. In our previous study [4], if the extractive content in the pulp was kept the same, after higher temperature pretreatment, the bleachability of the pulp was higher. The higher bleachability of pulps after multistage chip flashing may due to the long-time high temperature pretreatment. The condensate collected from chip flashing was heavily contaminated by the black liquor. The extractive content of the condensate in chip flashing was therefore not determined.

Presteamng

In the following study, presteaming was conducted to lower the extractive content of softwood chips just before the pretreatment. In the presteaming treatment, the chips were immersed with pure water. After heating up the water and chips to 160°C, a gas-off was performed for 30 minutes. Then the water was drained and the chips were treated with the white liquor charged with NaOH and Na₂S. No gas-off was performed any more after the chemicals were added. The results from regular gas-off process at 140°C were used as the reference.

Table 6-5. Effect of Pre-steaming on Extractive Content and Bleachability of Pulps
(20g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

Treatment	Gas-off Temp(°C)	Kappa Number	Brightness (% ISO)	TEC (%)	NEC (%)
None	140	23.2	87.1	0.35	0.09
Presteamng	None	22.8	87.3	0.38	0.05

TEC: Total Extractive Content

NEC: neutral Extractive Content

As mentioned before, in the presteaming case, when there was no active alkali added to the liquor, more extractives and more neutral extractives were removed from the system by the gas-off process [4]. This is equivalent to a steaming process to lower the extractive content before the regular treatments. After the pretreatment and cooking stages, less amount of extractives stayed in the pulps. As shown in Table 6-5, compared to the reference case, though no gas-off was performed in the regular pretreatment, comparable bleachability of pulps was achieved. Shown in Table 6-6, compared to the reference case, in the presteaming treatment, the neutral extractive content was lower in both chips and black liquor after the pretreatment, which resulted in a higher bleachability of the pulp. The bleachability of the presteamed pulp could be further enhanced if we conducted another gas-off during the charged pretreatment. So, the ideal operating conditions of the pretreatment with a high temperature gas-off process to get enhanced bleachability should include a presteaming treatment before the charged liquor pretreatment.

Table 6-6. Effect of Presteaming on Neutral Extractive Content
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

		After Pretreatment before Cooking		
Treatment	Gas-off Temperature	NEC in Chips (%)	pH of Black Liquor	NEC in Black Liquor (%)
None	140°C	0.069	11.43	0.0177
Presteaming	None	0.055	11.45	0.0171

Effects of WLP

As found in our previous experiments [4], more extractives could be removed by the pretreatments with a high temperature and a low alkalinity. However, more extractives could be suspended in the pretreatment liquor with a high pH value during a low temperature gas-off. To balance these two situations,

white liquor profiling is a practical method to remove more extractives with a high-temperature gas-off while keep a high pH value of the pretreatment liquor to prevent the precipitation of extractives on the fibers. Two cases of WLP were studied and results are shown in Table 6-7. In one case, the white liquor was added to the pretreatment before the gas-off process, i.e., at the very beginning of the pretreatment. In the other one, the white liquor was added to the pretreatment liquor right after the gas-off process. The case with gas-off at 140°C was used as a reference.

The bleaching results indicated that compared to the reference case, comparable bleachability in the high temperature gas-off process with WLP could be achieved. With WLP the pulps had comparable neutral extractive content and lower total extractive content, compared to the reference case.

Table 6-7. Effect of White Liquor Profiling on Extractive Content and Bleachability of Pulps
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

White Liquor Profiling	Gas-off Temperature	Kappa Number	Brightness (% ISO)	TEC (%)	NEC (%)
None	140°C	23.2	87.1	0.35	0.09
Before Gas-off	160 °C	23.4	86.9	0.20	0.08
After gas-off	160 °C	24.5	87.4	0.21	0.08

For the cases with WLP before the gas-off, the pH value of pretreatment liquors was increased, even higher than that in the reference case. Smaller amounts of extractives would precipitate on the fiber surface. Therefore, the total extractive content in pulps was lower. On the other hand, since the gas-off was performed at a higher temperature, a greater amount of extractives was removed by the gas-off process, as shown in Table 6-8. These two factors enhanced the bleachability of pulps.

For the case with WLP after the gas-off operation, the pretreatment stage before the end of the gas-off operation was exactly like the pretreatment at a high temperature without WLP. As found in our previous study, during the pretreatment, with a high gas-off temperature, more alkali was consumed. There was a larger drop in the pH value of the system. More extractives can be removed by the gas-off because of the low pH value of the pretreatment liquor. After WLP, the pH value of the pretreatment liquor was increased before the displacement. Some of the neutral extractives reprecipitated on the fiber surface would be re-suspended in the liquor. After the cooking liquor displacement, more extractives were removed with the displaced black liquor. WLP after the gas-off might result in better pulp bleachability.

Table 6-8. Effect of White Liquor Profiling on Neutral Extractive Content
(20g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

White Liquor Profiling	Gas-off Temp (°C)	After Pretreatment Before Cooking					
		Condensate			Black Liquor		Chips
		pH	TEC(%)	NEC(%)	PH	NEC(%)	NEC(%)
None	140	6.89	0.0356	0.0162	11.43	0.177	0.069
Before Gas-off	160	6.95	0.0391	0.0166	12.43	0.188	0.059
After Gas-off	160	6.27	0.0408	0.0178	12.47	0.194	0.043

Pretreatment with Black Liquor

In a real batch extended delignified kraft cooking, the chips were pretreated with all kinds of black liquors in different stages, such as warm black liquor, hot black liquor and washing filtrate. In this study, the effect of the black liquor pretreatments was also considered. The simplified extended delignified cooking process with only one pretreatment was still used. In the pretreatment,

the temperature and alkali concentration were similar to those of the hot black liquor pretreatment in a real batch extended delignified process. The pulp bleachability and the extractive content of pulps and the condensate are listed in Table 6-9 and 6-10. It seemed that the gas-off process had little effect on the bleachability and the extractive content of the pulps. The gas-off temperature also had little effect. The composition of the condensate indicated that the amount of extractives removed by the gas-off process was much lower than that from the pretreatment with white liquors. During the black liquor pretreatment, a lot of foam was generated. The amount of foam depended on the pH value, the dissolved solid content and the tall oil content of the black liquor. During the gas-off process, the foam may block the releasing of volatile organics or adsorb the organics from the vapor. Less than 0.5% of the total extractives and less than 3% of the total neutral compounds in chips were removed during the gas-off process, about one third as much as in the cases with white liquor pretreatments. Similar to white liquor pretreatments, at a higher gas-off temperature, more extractives were removed when gas-off. But, the difference in the neutral extractive content in the condensate between the high temperature gas-off and the low temperature gas-off was very small. On the other hand, due to their high dissolved organic solid content, the black liquors were much better buffered systems than white liquors. Therefore, the difference in the pH of black liquors between the high temperature pretreatment and the low temperature pretreatment was not as large as in the white liquor pretreatments. The low removal efficiency of the neutral extractive compounds and well buffered black liquors made the gas-off process have almost no effect on the bleachability of pulps.

Table 6-9. Effect of Gas-off Temperature and White Liquor Profiling on Extractive Content and Bleachability of Pulp (Black Liquor Pretreatment)

White Liquor Profiling	Gas-off Temp(°C)	Kappa Number	Brightness (% ISO)	TEC (%)	NEC (%)
None	None	23.6	86.0	0.40	0.16
None	130	22.3	86.2	0.30	0.17
None	160	23.4	86.3	0.35	0.13
Before Gas-off	160	22.9	86.7	0.33	0.08
After Gas-off	160	23.0	86.5	0.27	0.11

Table 6-10. Effect of White Liquor Profiling on Neutral Extractive Content (Black liquor pretreatment)

White Liquor Profiling	Gas-off Temp (°C)	After Pretreatment Before Cooking				
		Condensate			Black Liquor	Chips
		pH	TEC(%)	NEC(%)	pH	NEC(%)
None	None	N/A	N/A	N/A	12.70	0.209
None	130	7.15	0.0075	0.0046	12.74	0.184
None	160	6.88	0.0097	0.0048	12.67	0.163
Before Gas-off	160	7.03	0.0077	0.0048	12.84	0.115
After Gas-off	160	6.88	0.0097	0.0048	12.94	0.110

The WLP results indicated that after WLP, the pH of the pretreatment liquors was increased. As a result, the neutral extractive content in the chips after the pretreatment and final pulps was lowered. The bleachability of the pulps with WLP was enhanced. Due to the low removal efficiency of the neutral extractive compounds by the gas-off process, about same amount of neutral extractive compounds was removed in both WLP cases. There was no

difference in the performance for WLP before or after the gas-off. Thus, WLP before the gas-off was more desirable because of the easier operations.

Effect of Washing Stage

It is known that after the caustic washing, the extractive content of kraft pulps is lowered and the pulp bleachability is improved [9]. In the real extended delignification process, one or two stages of caustic washing may be involved. Here, the effect of caustic washing with and without WLP was evaluated. As shown in Table 6-11, compared to the regular gas-off process, by adding a washing stage, the total extractive content of pulps was lower significantly, even in the cases with a high temperature pretreatment. If some of the white liquor was added to the washing stage to enhance the washing, the neutral extractive content of pulps was further lowered and the bleachability was improved. For WLP to the pretreatment stage and to the washing stage, there was no big difference in the bleachability of the pulps.

Table 6-11. Effect of Washing Stage on Extractive Content and Bleachability of Pulps
(20g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

Washing	Gas-off Temp(°C)	Kappa Number	Brightness (% ISO)	TEC(%)	NEC(%)
None	140	23.2	87.1	0.35	0.09
Without WLP	160	24.0	86.9	0.14	0.10
With WLP	160	24.4	87.5	0.12	0.02
WLP to Pre	140	23.7	87.4	0.18	0.05

* Instead to the washing stage, WL in WLP was sent to the pretreatment stage

Similarly, in the cases with the black liquor pretreatment, compared to the regular gas-off process, by adding a washing stage, the total extractive content and the neutral extractive content of pulps was lower significantly and the

bleachability was improved (shown in Table 6-12). If some of the white liquor was added to the washing stage, such enhancement was further strengthened. WLP to the washing stage resulted in even lower extractive content and better bleachability of pulps than WLP to the pretreatment stage in the cases of black liquor pretreatments.

Table 6-12. Effect of Washing Stage on Extractive Content and Bleachability of Pulps
(Black liquor pretreatment)

Washing	Gas-off Temp(°C)	Kappa Number	Brightness (% ISO)	TEC (%)	NEC (%)
None	160	23.4	86.3	0.35	0.13
Without WLP	160	22.3	86.7	0.29	0.07
With WLP	160	22.6	87.3	0.27	0.04
WLP to Pre	160	23.0	86.8	0.30	0.07

* Instead to the washing stage, WL in WLP was sent to the pretreatment stage

Effect of the Gas-off Time

Not only the gas-off conditions but also the gas-off time are very important. It is easy to understand that the longer the gas-off time, the larger the amount of extractives that can be removed from the system. Figure 6-1 shows the gas-off process when pretreated with either black liquors or white liquors at different temperatures (130°C and 160°C). The white liquor and the black liquor had the same active alkali charge and sulfidity at the beginning of the pretreatments. The condensate was collected at a constant interval (5 minutes) and the extractive content was measured.

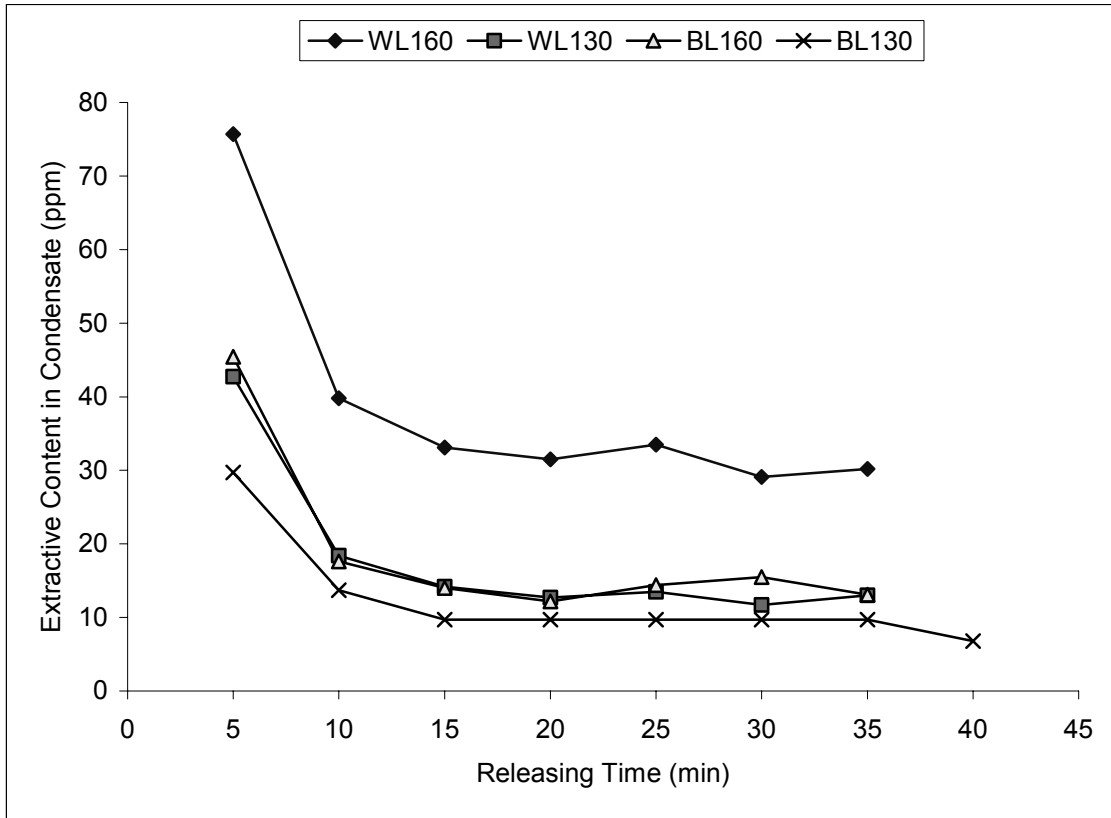


Figure 6-1. Extractive Content in the Condensate (ppm, Based on OD chips)

More extractive was removed during the first several minutes of gas-off. Then the rate of the extractive removal became constant. More extractive was removed when pretreated with white liquor than with black liquor. In both cases (pretreated with WL and BL), the higher the temperature, the greater the amount of extractive that could be removed during the gas-off process. The longer the gas-off time, the higher the amount of extractives can be removed. However, the gas-off time could not be too long. Otherwise the pH value of the pretreatment liquor would drop too much and it would change the extractive distribution in the system, and finally affected the extractive content of the pulp. 20 – 25 minutes of gas-off was sufficient.

Effect of Two-Stage Pretreatment

All our previous results were based on one-stage pretreatment, and a general tendency was presented. In the real world, there are two to four stages of pretreatment in the batch extended cooking. Results may be different if there were two or more stages of pretreatment. The previous stages of pretreatment will affect the pH of the last stage of pretreatment in some aspects, such as removing free acidic compounds from the chips, initiating peeling reactions, and thus affect the distribution of extractives between the black liquor and the chips. In this section, cooks with two-stage pretreatment were performed and the one-stage pretreatment with low temperature gas-off was used as a reference.

Based on two aspects, more extractives may be removed if the gas-off is performed in the first stage of pretreatment. First, the chips in the first stage of pretreatment are untreated fresh chips. The concentration of extractives is relatively high in the chips. Second, the black liquor in this stage is recycled from previous cooks and has gone through the stages of cooking, hot black liquor treatment and warm black liquor treatment. It is the black liquor with the highest concentration of extractives of all the liquors in an extended delignified cook. However, the extractive distribution in the last stage of pretreatment seemed to have the largest effect on the cooking stage [3]. That black liquor will be recycled and reused in the next cook. Therefore, the properties of the black liquor in the last stage of pretreatment will not only affect the current cooking, but also affect the later cooks before it is finally sent to the evaporator. It may be more efficient to perform gas-off in the last stage of pretreatment. In this paper, for all two-stage processes, the gas-off was performed in the second pretreatment stage, the hot liquor pretreatment.

Table 6-13. Effect of Gas-off Temperature on extractive content and Bleachability of Pulps with Two-Stage Pretreatment (White Liquor Pretreatment)

Pretreatment	Gas-off Temp(°C)	Kappa Number	Brightness (% ISO)	TEC(%)	NEC(%)
2-stage	None	24.3	87.7	0.28	0.08
2-stage	140	23.6	87.9	0.27	0.06
2-stage	160	24.0	88.4	0.21	0.06
1-stage	140	23.2	87.1	0.35	0.09

Table 6-13 shows the final brightness and the extractive content of the pulps after a two-stage pretreatment. Compared to the one-stage pretreatment, more extractives were removed due to the extra stage of white liquor pretreatment and a higher total active alkali charge in the pretreatment. Therefore, the pulps from a two-stage pretreatment were much easier to bleach than the pulps from one-stage pretreatment. For all two-stage pretreatment, during the pretreatment with a gas-off process, some of the extractives were removed from the pulping system, which resulted in modifying the bleachability and extractive content of pulps. When the gas-off is performed at a higher temperature, the pulps resulted in a lower extractive content and a higher bleachability than those from low temperature gas-off processes.

Table 6-14. Distribution of Neutral Extractives after Two-Stage Pretreatment before Cooking

Gas-off Temp(°C)	First Stage		Second Stage		Condensate			Chips
	pH of BL	NEC of BL(%)	pH of BL	NEC of BL(%)	pH	TEC (%)	NEC (%)	NEC of Chips(%)
None	11.34	0.0148	12.47	0.0154	N/A	N/A	N/A	0.061
140	11.30	0.0141	12.61	0.0157	7.12	0.0196	0.0112	0.057
160	11.41	0.0146	12.49	0.0149	6.97	0.0264	0.0169	0.049
140	11.43	0.0177	N/A	N/A	6.45	0.0356	0.0162	0.069

Table 6-14 shows the neutral extractives distribution among the warm liquor, hot liquor, condensate and chips after the pretreatment before cooking. The one-stage pretreatment was used as a reference. After the first stage of pretreatment, some of the alkali was consumed due to the removal of the free acidic compounds and peeling reaction. During the second stage of pretreatment, less alkali was consumed compared to the one-stage pretreatment. The difference in the pH of the hot black liquor between high temperature and low temperature gas-off pretreatment was only 0.12, compared to 0.91 for one-stage pretreatment and gas-off. The neutral extractive distribution in the hot black liquor and chips in all the cases of two-stage gas-off were affected slightly by the pH difference. However, when the gas-off was performed at a high temperature, more extractives and neutral extractives were removed by the gas-off process. Therefore, the pulps prepared by a high temperature gas-off pretreatment had a relatively low extractive content and a high bleachability. About one fourth of the neutral extractives and a large amount of acidic compounds were removed by the warm liquor pretreatment. When the gas-off is done during the second pretreatment stage, relatively small amount of total extractives and neutral extractives could be removed by the gas-off process. Neutral extractives occupied a relatively large fraction of extractives in the condensate, which made the pH of the condensate higher than that from the one-stage gas-off pretreatment.

It is obvious that if the total active alkali charge in the one-stage pretreatment increases, the difference in the final pH of the pretreatment liquor after the gas-off will decrease. Therefore, if all the active alkali in the two-stage pretreatment is combined and put into a one-stage pretreatment, the one-stage pretreatment may not be sensitive to the pretreatment temperature and the pulp properties are somehow similar to the pulp prepared from the two stage pretreatment process. However, the two-stage process is more desirable since splitting the total active alkali charge into two stages levels out the alkali concentration in the pretreatment. In addition, one more stage of displacement

will reduce the extractive content in the pulping stage and lower the final extractive content of the pulp.

Conclusion

It is possible to modify the bleachability and the extractive content of batch extended delignified pulps with the high temperature gas-off process in the pretreatment. The results of the present study can be summarized as follows:

- Presteaming, white liquor profiling (WLP) and caustic washing were three efficient methods to enhance the performance of high temperature gas-off process.
- For the pretreatment with white liquors, using the modified high temperature gas-off process significantly lowered the extractive content, especially the neutral extractive content of pulps. Presteaming, WLP to the pretreatment liquor after gas-off, WLP to the washing liquor were found to lower the extractive content and improve the bleachability of the extended delignified pulps.
- For the pretreatment with black liquors, the gas-off process had little influence on the extractive content and the bleachability of pulps. WLP to the pretreatment liquor and WLP to the washing liquor were found to improve the bleachability of pulps.
- More extractives were removed when pretreated with white liquors than with black liquors.
- More extractives were removed during the first several minutes of the gas-off process. Then, the rate of the extractive removal leveled off.

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CHAPTER VII

Influence of Pretreatment with Gas-off on the Extractive Content and Bleachability of Extended Delignified Hardwood Kraft Pulps

Abstract

The objective of this study is to investigate the impact of pretreatment with gas-off on the extractive content of batch extended delignified hardwood kraft pulps. Due to the involvement of black liquor impregnation stages in regular batch extended delignification processes, it is very possible for extractives to accumulate in the black liquor and precipitate on the fiber surface, and thus affect the bleachability of extended delignified kraft pulps. During the pretreatment stage, if some vapor is released (gas-off process), some volatile compounds may be removed with the vapor. A simplified extended delignification process, with only one pretreatment stage and no post-treatment, was used in this study to determine the effect of pretreatment conditions on the bleachability and extractive content of the southern red oak kraft pulps. Both white liquors and black liquors were used in the pretreatment and the gas-off process was included. Using the gas-off process lowered the extractive content, especially the neutral extractive content of pulps. Up to 11% of the neutral wood extractive compounds and up to 3% of the wood extractives could be removed from the system during the gas-off in some cases. The operating conditions of the gas-off process, such as gas-off temperature, pretreatment alkalinity and sulfidity, affected the extractive removal efficiency and the extractive content of pulps, and finally affected the bleachability of pulps. High gas-off temperature, high sulfidity and high alkalinity in the pretreatments were found to enhance the bleachability of pulps. More extractives were removed by the gas-off process when pretreated with the white liquor than with the black liquor. The precipitation of the extractive compounds onto the fiber surface during the black liquor pretreatment increased the extractive content of the pulp and lowered the bleachability.

Keyword

Alkalinity, black liquor, bleachability, extended delignification, extractive content, gas-off, hardwood, kraft pulping, pretreatment, sulfidity, temperature

Introduction

In the previous study about the influence of the pretreatment with a gas-off process on the properties of the softwood kraft pulps, it was found that when a gas-off process in the pretreatment stage was introduced, some of the extractives from the digester could be removed from the digester [1]. The extractive content of the pulp was lowered and the bleachability was thus enhanced. Neutral extractive compounds seemed to have a more pronounced effect on the pulp bleachability. During the gas-off process, volatile neutral extractive compounds were concentrated in the gas-off condensate. More extractive compounds could be removed when the gas-off operation is performed under the combination of a higher pretreatment temperature, lower alkali concentration and higher sulfidity. More extractives were removed by the gas-off when the chips were pretreated with white liquor than with black liquor [2].

For hardwoods, the extractive content, especially the neutral extractive content, is usually higher than that in softwoods. During the gas-off, it was expected to remove relatively more neutral extractives. The change in the neutral extractive content in hardwood kraft pulps after the gas-off pretreatment may be much higher than that in softwood kraft pulps. Therefore, the gas-off process is expected to have larger influence on the bleachability of hardwood kraft pulps than on that of softwood pulps.

The amount of extractives removed by the gas-off process not only depends on the extractive content in the wood chips, but also depends on the volatility of the extractives. The volatile natural compounds in woods are mainly terpenes [3,4], small molecular organic acids [3] and some aromatic compounds [4]. In pines, the oleoresin is the dominant resin type in which monoterpenoids

and diterpenoids are dominant constituents. In hardwood, the parenchyma resin is dominant which contains triterpenoids and steroids[5]. The higher molecular weight of resins in hardwoods make them less volatile and harder to be removed by the gas-off process. Studies found that the main emissions of volatile organic compounds (VOCs) were terpenes from softwood and acetic acid from hardwood [3]. The amount of other volatile compounds in hardwood is very small[5]. Therefore, due to the low volatility of the neutral compounds in the hardwood, it is expected that the gas-off process may have little effect on the extractive content and bleachability of extended delignified hardwood kraft pulps.

The objective of this study is to determine the possibility of lowering the extractive content, especially those unsaponifiable extractive compounds in the hardwood kraft pulps by including a gas-off process in the pretreatment. A simplified extended delignification process, with one stage of pretreatment and no post treatment, was used. The effects of the following operating variables were studied: 1) gas-off temperature, 2) alkalinity, 3) sulfidity. The effect of the black liquor pretreatment was also studied.

Experimental

Raw Materials

A 30-year old southern red oak tree grown in Raleigh, North Carolina, USA, was used in this study. The wood logs were debarked and chipped. The chips with around 50% moisture content (wet basis) were screened. The accepted fraction with the size between 1” and 5/8” and with the thickness under 8 mm was used. The chips were kept fresh in the cooler to prevent the loss of extractives. The extractive contents of the wood were determined as following:

Total extractive content:	1.12%
Neutral extractive content:	0.19%

The hardwood black liquor was generated in our lab. The properties of the black liquor were determined as following:

pH:	12.9
Dissolve Solid Content:	14.1%
Total Titratable Alkali:	31.5 g/L as Na ₂ O
Active Alkali:	14.6 g/L as Na ₂ O
Sulfidity:	52%

Pulping

The simplified extended delignification process was described elsewhere [1]. The target kappa number for hardwood kraft pulps was 9. The cooking conditions are described in Table 7-1.

Table 7-1. Conditions of Extended Kraft Cooking for Hardwood

	Pretreatment Stage	Cooking Stage
Active Alkali Charge, as Na ₂ O	0 – 21g/L	18%
Sulfidity	60 %	25%
Liquor Volume	4.5L	2.5L Cooking WL
Gas-off Temp	120 - 160 °C	None
Temp Increasing Rate	100°C/hr	100°C/hr
Maximum Temperature	160°C	170°C
Time at Maximum Temp	20 minutes	To desired H-factor

For the processes with the black liquor pretreatment, 3.5 liters of black liquor was used in the pretreatment stage. The active alkali charge and the sulfidity of the liquor at the beginning of the pretreatment were adjusted to 20g/L as Na₂O and 60%, respectively, by adding a certain amount of white liquor.

Bleaching

Bleaching was conducted in high density polyethylene(HDPE) bags by mixing pulps and bleaching chemicals together. These bags were sealed and put into a water bath set at 70°C. The bleaching sequence D(E+P)D was used. The operating conditions used in the bleaching process are listed in Table 7-2. The final brightness of the pulp was measured according to the ISO standard.

Table 7-2. Process Conditions for Bleaching

Stage	Time(mins)	Temp(°C)	Consistency	Chemical Charge	Final pH
D ₀	60	70	10%	K.F. = 0.20	
E + P	60	70	10%	NaOH = 1.5% H ₂ O ₂ = 0.5%	10.3 – 10.9
D ₁	180	70	10%	ClO ₂ = 1.0%	3.5 – 4.0

Extraction and Fractionation

The procedure to determine the extractive content and neutral extractive content of wood meal and pulps is described elsewhere [1]. The measurement of the neutral extractive content in hardwood black liquors was not accurate. The repeatability was very poor. Therefore, the extractive content in the black liquor was not measured in all cases.

Results and Discussion

Effect of Gas-off Temperature

During the pretreatment with a gas-off process, some of the volatile extractive compounds were removed from the pulping system, which resulted in modifying the bleachability and the extractive content of kraft pulps. The bleachability and extractive content of pulps are shown in Table 7-3 for different gas-off temperatures. In all gas-off cases, the bleachability of the pulps

increased by 0.1 – 1.1% ISO and the extractive content of the pulps decreased by up to 0.1 – 0.2%. The neutral extractive content of the pulps also decreased by up to 0.1%. The higher the gas-off temperature, the more neutral extractive compounds could be removed by the gas-off process. Therefore, higher temperature gas-off process should have resulted in lower neutral extractive content in the pulps. On the other hand, the higher the pretreatment temperature, the larger drop in the pH of the black liquor after the pretreatment [6], which made the extractives or lignin fragments in the black liquor easier to precipitate onto the fiber. The precipitation increased the total extractive content of the pulp after high temperature pretreatment.

Table 7-3. Effect of Gas-off Temperature on Extractive Content and Bleachability of Pulps
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

Gas-off Temp(°C)	Brightness (% ISO)	NEC(%)	TEC(%)
None	88.7	0.37	0.85
120	88.8	0.35	0.66
135	89.1	0.34	0.72
150	89.4	0.28	0.73
160	89.8	0.28	0.78

TEC: Total Extractive Content

NEC: Neutral Extractive Content

The extractive content of the gas-off condensate was also studied. Similar to the softwood gas-off process, the condensate was a strong-smelling, cloudy, nearly neutral pH water/organics mixture with the color ranging from clear lightly yellowish to milky white. At a high gas-off temperature, the condensate was cloudy, milky white mixture. After storing for a period of time, the pH of the condensate decreased slightly, about 0.3 – 0.4 pH. At a low gas-off temperature, the condensate was clear, transparent liquid, with color ranged from slightly

yellow to tan, which may be due to the contamination of the black liquor. The properties of the condensate are shown in Table 7-4. Up to 3% of the total extractives and up to 6% of the neutral compounds were found in the condensate. The extractive compounds in southern red oak were not very volatile at low temperature. At a low gas-off temperature (below 150°C), only a small portion of the extractives was removed by the gas-off process. When the gas-off temperature increased, the amount of extractive removed by the gas-off process increased dramatically. At a high gas-off temperature, more extractives came out with the condensate. More neutral extractives also came out. The percentage of the neutral fraction in the condensate extractives decreased, which was due to the higher volatility of small molecular organic acids in hardwoods [7]. A lower pH condensate resulted from a high gas-off temperature.

Table 7-4. Effect of Gas-off temperature on Extractive Content of Gas-off Condensate
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

Gas-off Temp(°C)	pH	NEC(%) (Based on Chip)	TEC(%) (Based on Chip)	Neutral Fraction of Condensate Extractives
120	8.02	0.0036	0.0056	64%
135	7.53	0.0042	0.0066	64%
150	6.26	0.0098	0.0186	53%
160	5.89	0.0152	0.0302	50%

In the gas-off process using softwood, at a high pretreatment temperature, the pH of the black liquor at the end of the pretreatment decreased dramatically, which affected the distribution of the neutral extractive compounds between the black liquor and the pulps. With a lower final pH of the black liquor, more extractives stayed with the pulps, which resulted in a higher extractive content and a lower bleachability of the pulps. The properties of the black liquor after the pretreatment are listed in Table 7-5.

Table 7-5. Extractive Content vs. Final pH of Black Liquor
(20 g/L AA as Na₂O, 60% sulfidity, white liquor pretreatment)

After Pretreatment before Cooking		
Gas-off Temperature(°C)	NEC in Chips (%)	pH of Black Liquor
None	0.189	10.07
120	0.188	10.45
135	0.177	10.34
150	0.156	10.13
160	0.129	10.11

The fatty acid and resin acid content in hardwoods is much lower than that in softwoods. The amount of neutral compounds suspended in the black liquor by the micelle formation mechanism [8] during hardwood kraft pulping is expected to be low. Therefore, the neutral extractive content in the hardwood chips after the pretreatment may not be as sensitive to the final pH of the black liquor as in softwood cases. As shown in Table 7-5, comparing the case of gas-off at 120°C with the case without the gas-off, there was 0.38 difference in pH. However, the neutral extractive content in the chips was about the same. When the gas-off temperature increased, much more neutral extractives were removed. Although the final pH of the black liquor decreased, the neutral extractive content in the chips after pretreatment decreased due to the amount of neutral compounds removed by the gas-off process. On the other hand, the largest difference of final pH of the black liquor between the high temperature pretreatment and low temperature pretreatment was only 0.3, much smaller than in the corresponding softwood cases, which was more than 0.8 [1]. Therefore, the neutral extractive content in the pulps was not very sensitive to the pretreatment temperature. Thus, the bleachability of the pulp favored a high gas-off temperature.

Effect of Pretreatment Alkalinity

The effect of the final pH in the pretreatment can be more clearly seen in the following study. The active alkali charges in the pretreatment varied from 0 g/L to 20 g/L as Na₂O, but the sulfidity was kept at 60% in all cases. Table 7-6 shows the bleachability and extractive content of the pulps after the gas-off with different alkalinity. The process without the gas-off was used as a reference. When the active alkali charge in the pretreatment increased, the bleachability of the pulps increased. At the same time, the total extractive content in the pulps decreased. The neutral extractive content in the pulps after an alkaline pretreatment was lower than that in the pulps without the alkaline pretreatment. When pretreated with 0 g/L active alkali charge (pure water), the bleachability of the pulp had almost no improvement when compared with the reference case.

Table 7-6. Effect of Pretreatment Alkalinity on Extractive Content and Bleachability of Pulps (60% sulfidity, white liquor pretreatment with gas-off at 160°C)

Gas-off	AA (g/L as Na ₂ O)	Brightness(% ISO)	NEC(%)	TEC(%)
Yes	0	88.8	0.35	0.95
Yes	10	89.6	0.26	0.84
Yes	20	89.8	0.28	0.78
None	20	88.7	0.37	0.85

The extractive contents of the condensate after the pretreatment are shown in Table 7-7. Unlike the softwood cases, when the hardwood chips were pretreated without alkali charge, the gas-off process removed a relatively smaller amount of extractives. Due to the high acidity of the oak wood [9] and volatility of the acidic compounds [3], a substantial portion of the removed extractives belonged to acidic compounds. Only a very small amount of the neutral compounds, about 2.5% of the total neutral extractive content in the original chips, was removed. When the hardwood chips were pretreated with alkali

charge, even with a small amount of alkali charge, the amount of neutral compounds in the condensate increased substantially. This phenomenon indicated that the natural neutral compounds in oak wood were not very volatile, even with 160°C pretreatment. Most of the volatile neutral compounds were generated after the saponification reaction. The lower the alkalinity in the pretreatment, the greater the amount of extractive that came out during the gas-off. The amount of neutral extractive compounds that came out is also higher.

Table 7-7. Effect of Alkalinity on Extractive Content of Gas-off Condensate
(60% Sulfidity, white liquor pretreatment with gas-off at 160°C)

Active Alkali (g/L as Na ₂ O)	pH	NEC (%)	TEC (%)	NF (%)
0	4.41	0.0048	0.0234	21%
10	5.09	0.0170	0.0332	51%
20	5.89	0.0152	0.0302	50%

TEC: total extractive content, based on chip

NEC: neutral extractive content, based on chip

NF: Neutral Fraction of Condensate Extractive

As shown in Table 7-8, for the pretreatment with a low active alkali charge, the pH value of the black liquor was low. More extractives or lignin fragments precipitated on the fiber surface under the low alkali conditions instead of suspending stably in the pretreatment liquor. Even with the same neutral extractive content, the alkaline soluble extractive content in the pulp was high after a low alkalinity pretreatment. In a previous study [10], it was found that due to the thick cell wall of softwood kraft pulps, the diffusion played an important role in determining the bleachability. The diffusion was mainly affected by the neutral extractive content in the kraft pulps. For hardwood kraft pulps, due to the thin cell wall, the diffusion was not as important as in softwood pulps. The

reaction of extractives with the bleaching chemicals was very important. The alkaline soluble extractives may be more reactive than the neutral compounds. Therefore, this portion of extractives may affect the bleachability of the pulp more significantly than the neutral compounds. As a result, to maintain a high bleachability of kraft pulps, the alkalinity in the pretreatment should be high.

Table 7-8. Extractive Content vs. Final pH of Black Liquor
(60% sulfidity, white liquor pretreatment with gas-off at 160°C)

After Pretreatment Before Cooking			
Gas-off	AA(g/L as Na ₂ O)	NEC in Chips(%)	pH of Black Liquor
None	20	0.189	10.07
Yes	0	0.180	4.72
Yes	10	0.126	9.11
Yes	20	0.129	10.11

Effect of Pretreatment Sulfidity

Sulfidity in the pretreatment also affected the bleachability and extractive content of pulps. Since the sulfidity change will affect the final pH of the black liquor. The final pH then affects the precipitation of extractives, which in the end affects the extractive content and bleachability of the kraft pulps. The effect of the sulfidity is thus complicated and hard to observe. To eliminate the effect of the final pH, in this part of study, the active alkali charge in the pretreatment was adjusted so that the final pH of the black liquor after the pretreatment was kept around 10.1. As listed in Table 7-9, three different levels of sulfidity were chosen to determine its influence. The process without the gas-off was used as a reference.

Table 7-9. Effect of Pretreatment Sulfidity on Extractive Content and Bleachability of Pulps
(White liquor pretreatment with gas-off at 160°C)

Gas-off	AA (g/L as Na ₂ O)	Sulfidity (%)	Brightness (% ISO)	NEC (%)	TEC (%)
None	20	60	87.7	0.37	0.85
Yes	16	25	87.6	0.34	0.67
Yes	18.5	50	88.1	0.31	0.63
Yes	21	75	89.0	0.27	0.58

When pretreated under a higher sulfidity, the resulting pulps had a higher bleachability, lower total extractive content and neutral extractive content. As shown in Table 7-10, with the increase of sulfidity, the gas-off process removed more extractives. For the pretreatment with 75% sulfidity, a large amount of extractives and neutral compounds was removed by the gas-off process, more than 10% of the neutral compounds in the original chips were removed. The high bleachability of the kraft pulp after the high sulfidity gas-off was due to the high extractive removal efficiency. On the other hand, when chips are treated with high sulfidity liquor, the delignification process is more selective [11,12]. The residual lignin may be more reactive. Studies indicated that after a high sulfidity pretreatment before the kraft pulping the bleachability of the pulp was improved [13]. The higher bleachability was likely to be partly due to the structural modification of the residual lignin after the pretreatment with the high sulfidity liquor.

Table 7-10. Effect of Sulfidity on Extractive Content of Gas-off Condensate
(White liquor pretreatment with gas-off at 160°C)

Sulfidity(%)	pH	NEC(%) (Based on Chip)	TEC(%) (Based on Chip)	Neutral Fraction of Condensate Extractives
25	6.47	0.0065	0.0132	50%
50	6.26	0.0078	0.0150	52%
75	5.66	0.0202	0.0352	57%

Since it is hard to measure the neutral extractive content in the black liquor accurately, the balance of the neutral compounds among the pulp, black liquor and condensate could not be got, as in the previous softwood studies [1]. It is hard to determine whether there were new neutral compounds generated during the high sulfidity pretreatment or not. However, since the final pH of the black liquor was kept about the same, it is assumed that the concentration of neutral extractives was the same in the black liquor in all cases. Therefore, comparing the neutral extractive content in the condensate and the chips after the pretreatment, the neutral extractive balance can be approximately evaluated. The neutral extractive content of chips after the pretreatment are listed in Table 7-11. After pretreatment, the chips lost about 25% of their weight. Therefore, for 1000 grams of original chips, the neutral extractive balance after the pretreatment for all the cases were:

75% sulfidity:

Neutral compounds: 1.27 g

50% sulfidity:

Neutral compounds: 1.41 g

25% sulfidity

Neutral compounds: 1.50 g

During the gas-off process, when the vapor came out of the digester, some compounds that are volatile only at a high temperature, were cooled down and condensed. They may stay in the valves or pipes before entering the condenser. There usually is some loss of extractives during the gas-off. The larger the amount of extractives was removed, the larger the loss that might result. From the material balance, there was no obvious indication that new neutral compounds were generated during the high sulfidity pretreatment.

Table 7-11. Extractive Content vs. Final pH of Black Liquor
(White liquor pretreatment with gas-off at 160°C)

After Pretreatment Before Cooking			
Gas-off	Sulfidity(%)	NEC in Chips(%)	pH of Black Liquor
None	60	0.189	10.07
Yes	25	0.191	10.12
Yes	50	0.178	10.07
Yes	75	0.142	9.99

Pretreatment with Black Liquor

In all the previous cases, only white liquors were used in the pretreatment. Real batch extended delignification processes usually involve at least one impregnation stage[14]. The black liquor collected from the previous cooks is used in that stage. In this study, the effect of the black liquor pretreatments was also considered. The pulp bleachability and the extractive content of pulps and condensates are listed in Table 7-12 and 7-13. Similar to the softwood cases, it appeared that the gas-off process had little effect on the bleachability and the extractive content of the pulps. The gas-off temperature also had little effect.

Table 7-12. Effect of Gas-off Temperature on Extractive Content and Bleachability of Pulps
(20 g/L AA as Na₂O, 60% sulfidity, black liquor pretreatment)

Gas-off Temp(°C)	Brightness (% ISO)	NEC(%)	TEC(%)
None	87.7	0.45	1.03
120	87.7	0.41	0.78
140	87.8	0.43	0.95
160	88.1	0.40	0.91

The compositions of the condensate are listed in Table 7-13. It is indicated that the extractive contents were much lower than that from the pretreatment with white liquor. Fewer than 1.5% of the total extractives and less than 5% of the neutral extractive compounds in chips were removed during the gas-off, about one half the amount of the corresponding cases with the white liquor pretreatment. At a low gas-off temperature, virtually no extractives were removed during the gas-off. On the other hand, due to high dissolved solid content of the black liquor, it was easier for the extractives in the black liquor to precipitate onto the fiber surface. Therefore, the total extractive content in the kraft pulps with the black liquor pretreatment was higher, and the bleachability of the pulps was lower than the corresponding white liquor pretreatment cases. For the processes with the black liquor pretreatment, only the high temperature gas-off is not sufficient to enhance the bleachability of the pulps. Thus, the gas-off should be used combined with other techniques such as white liquor profiling [15, 16].

Table 7-13. Extractive Content of Condensate and Chips after Pretreatment
(20g/L AA as Na₂O, 60% sulfidity, black liquor pretreatment)

Gas-off Temp(°C)	Condensate				After Pretreatment	
	pH	NEC(%)	TEC(%)	Neutral Fraction	pH of Black Liquor	NEC of Chips(%)
None	N/A				10.59	0.182
120	7.48	<0.0001	0.0021	N/A	11.01	0.180
140	7.08	0.0008	0.0029	28%	10.82	0.163
160	6.49	0.0082	0.0182	45%	10.53	0.158

Conclusion

It is possible to modify the bleachability and the extractive content of batch extended delignified hardwood kraft pulps by introducing gas-off in the pretreatment. The results of the present study can be summarized as follows:

- The pulp extractive content affected the bleachability of the extended delignified pulps.
- The gas-off process affected the extractive content and bleachability of the pulps.
- Most of the natural volatile substances in southern red oak were acidic compounds. Most of the volatile neutral compounds were generated by the saponification reactions and only volatile at high temperature.
- The conditions of the pretreatment in the extended delignification, such as the gas-off temperature, sulfidity, alkalinity affected the bleachability of pulps.
- High gas-off temperature, high alkalinity and high sulfidity in the pretreatment with the gas-off lowered the extractive content and resulted in high bleachability of pulps.
- More extractives were removed with a high temperature gas-off than at a low temperature and more extractives were removed when pretreated with a low

alkali charge than with a high alkali charge. Under the high sulfidity pretreatment, more extractives were removed by the gas-off process.

- Compared to the gas-off process in softwood cases, due to the low volatility of the natural neutral extractives in hardwood, the bleachability and extractive content of hardwood pulps were not very sensitive to the gas-off process. The extractive removal efficiency in hardwood gas-off process was lower.
- A small amount of extractives was removed when using pretreatments with black liquors. The gas-off process had no obvious effect on the extractive content and the bleachability of pulps.

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CHAPTER VIII

Bleachability of Kraft Pulps from Earlywood and Latewood of Fast-Grown Loblolly Pine

Abstract

In this study, the pulping and bleaching properties of the earlywood and latewood of a fast-grown southern pine were studied. Under the same pulping condition, the kappa number of the latewood kraft pulp was higher than that of the earlywood. At around the same kappa number, the yield of the latewood was higher than that of the earlywood. The bleaching results showed that the latewood kraft pulp had lower bleachability than the earlywood kraft pulp due to its thicker cell wall and slower leaching rate.

Keyword

Bleachability, Cell Wall Thickness, Coarseness, Earlywood, Kraft Pulping, Latewood, Leaching, Mature Wood, Softwood

Introduction

Due to the increasing environmental pressure, concerns regarding the environmental impact of bleaching plant effluent have resulted in the kraft pulping processes to undergo major modifications. During the last decades, the factors that affect the bleachability of kraft pulps, such as the residual lignin structure and extractives, have been the topics of intensive research. However, the fiber morphology, as a factor of determining the bleachability of kraft pulps, has rarely been studied.

Because of the increasing demand and decreasing supply of raw fiber materials, an increasing portion of wood available to the pulp and paper industry will come from young, fast-grown plantations. Wood produced under intensive plantation forestry will be different from extensively managed forestry. The fast grown plantation will increase the proportion of juvenile wood [1, 2, 3, 4] and

earlywood[5]. The characteristics of such wood and fiber will be different from older, natural stands of the same wood species. The ratio of juvenile wood to mature wood, earlywood to latewood will thus affect the quality of wood and properties of wood and fiber products. Therefore, gaining deep understanding of the juvenile wood, earlywood and latewood properties will help us with better evaluation of the quality of fast-grown wood and their utilization.

That the fibers from earlywood and latewood have different properties has been studied for many years. Previous studies have focused on the chemical composition [6, 7, 8], refining properties [8, 9], penetration properties [10] and handsheet properties [11]. The bleaching properties of the earlywood and latewood pulps were rarely studied. It is well known that the chemical compositions of earlywood and latewood are different. For loblolly pine, the earlywood has a higher extractive content [6] and higher lignin content [6, 7] than that of latewood. Higher percentage of tracheid lignin in earlywood existed in the middle lamella and the cell corner than in latewood [7]. These factors may make earlywood harder to bleach than latewood. On the other hand, the latewood fiber wall is much thicker than that of the earlywood fiber. The bleaching process is a combination of chemical reaction kinetics and diffusion dynamics of bleaching chemicals. It is therefore possible that the thick cell wall will retard the penetration of the bleaching chemicals into the cell wall or the diffusion of the lignin fragment out of the fiber wall, which may lower the bleachability of the latewood pulp.

In this study, a fast-grown loblolly pine tree was used and the earlywood and latewood of the mature wood were carefully separated. The pulping and bleaching properties of the earlywood and latewood were determined.

Experimental

Raw Material

A 20-year old fast-grown loblolly pine plantation grown near Raleigh, North Carolina was used in this study. Wood from chest high level to 10-foot

level was chosen for radial symmetry and for lack of compression wood. Mature wood was defined as that wood outside the inner eight rings. The wood of the outer 8 – 10 rings was used.

Chip Preparation

The log was debarked and cut into one-inch thick disks. The disks were cut into half-inch wide small pieces. The small pieces were immersed into water overnight before cutting. The earlywood and latewood zones in a ring became more distinct after soaking. The earlywood and latewood were carefully separated by a sharp knife. The latewood chips were carefully chopped so that they were almost pure latewood. The earlywood chips were mixtures of earlywood and latewood. The chips were air-dry to approximately 15% moisture content (wet basis) and stored in the refrigerator at 4°C. The properties of the earlywood and latewood chips were as follows:

Table 8-1. Wood Properties

	Earlywood	Latewood
Purity	~ 20 – 30% Latewood	< 5% Earlywood
Extractive Content	3.67%	1.66%
Neutral Extractive Content	0.16%	0.08%

Pulping

The kraft cooks were done in one 7L M&K digester vessel. The cooking conditions are described in Table 8-2. The target kappa number was 30.

Two cooks were done. In the first cook, equal amounts of earlywood and latewood chips were put into the same digester. The earlywood chips and the latewood chips were separated by a coarse iron screen. They were therefore cooked under the same conditions. The pulps prepared from earlywood and latewood were labeled as early-1 and late-1, respectively. In the second cook,

only latewood chips were put into the digester. The H-factor was adjusted so that the kappa number of the latewood pulp could match that of early-1. The pulp prepared from the second cook was labeled as late-2.

Table 8-2. Conditions of Kraft Cooking

Active Alkali Charge, as Na ₂ O	19%
Sulfidity	25%
Liquor Volume	L/W = 4.5
Temp Increasing Rate	100°C/hr
Maximum Temperature	170°C
H-factor	To target kappa number

Bleaching

Bleaching was conducted in high density polyethylene(HDPE) bags or oxygen oxidation bomb by mixing pulps and bleaching chemicals together at 70°C. The bleaching sequence D(Eop)DED was used. The operating conditions used during bleaching are listed in Table 8-3.

Table 8-3. Process Conditions for Bleaching

Stage	Time(mins)	Temp(°C)	Consistency	Chemical Charge	Final pH
D ₀	60	70	10%	K.F. = 0.23 NaOH ~ 2%	
E+P	60	70	10%	H ₂ O ₂ = 0.5% O ₂ = 30psi, 15min	10.3 – 10.9
D ₁	180	70	10%	ClO ₂ = 0.7, 1.0, 1.3%	3.5 – 4.0
E	60	70	10%	NaOH = 1.0%	10.3 – 10.9
D ₂	180	70	10%	ClO ₂ = 0.5%	3.5 – 4.0

Extraction and Fractionation

To determine the extractive content of wood meal and pulp, samples of wood chips and pulps were dried in a vacuum oven at room temperature overnight. The wood meals were prepared by grinding the wood chips in a Willey mill and sieving through a 40 mesh screen. 15 grams of wood meal or pulp were extracted for at least 10 hrs in a soxhlet with acetone. The solvents were removed by using a rotavapor. For wood meals, the extracts were hydrolyzed in a flask at 70°C for 4 hrs with 80ml 0.5N KOH/95% ethanol solution. Then the solution was diluted with 80ml water and the pH of the solution was adjusted to 13.2 ± 0.2 by KOH. The diluted solution was extracted in a separatory funnel with hexane three times, each with 50ml of hexane. The extractives in the hexane phase were labeled as the neutral fraction. Then the water phases were acidified to pH around 2.5 by adding 1N HCl and then extracted in a separatory funnel with chloroform three times, each with 50ml of chloroform. The extracts were labeled as the saponifiable fraction. The sum of the neutral fraction and the saponifiable fraction was the total extractive content of the sample. For pulps, only the total extractive content was determined.

Leaching

Leaching measurements were conducted in 1.0 liter PVC bottles. 10 grams of pulp was used in each experiment. The pulp was mixed with NaOH solution in the bottle and the bottle was sealed. The bottle was put in the water bath under controlled temperature. The operating conditions are listed in Table 8-4.

Table 8-4. Process Conditions for Leaching

Pulp	10g
NaOH Charge	0.01M
Consistency	1%
Temperature	70°C
Starting pH	11.8

After a period of time, about 15 ml solution was taken out from the bottle by a syringer. The solution was cooled down to the room temperature, filtered. The amount of lignin dissolved during the alkaline treatment was measured by UV at 280nm using a molecular extinction coefficient of 20 l/g-cm [12]. Leachability measures the diffusion rate of the bulky lignin out of the fiber wall. Since the extractive molecules are smaller than lignin molecules, they are much easier to leach. Some of the extractives have absorbance at 280nm. Therefore, the existence of extractives will affect the accuracy of the lignin leaching measurement. To exclude the effect of extractives, all the pulps were extracted by organic solvents before leaching measurement.

Fiber Analysis

The fiber length and coarseness were determined by Fiber Quality Analyzer (OpTest Equipment Inc.)

Results and Discussion

Pulp Properties of Earlywood and Latewood

Generally, latewood from loblolly pine has higher cellulose content [6, 13] and lower lignin content [6, 13, 14, 15] than the earlywood. The properties of kraft pulps from earlywood and latewood were listed in Table 8-5. At about the same kappa number, the yield of latewood is much higher than that of the earlywood. This result confirmed the former studies on kraft pulping of loblolly

pine earlywood and latewood [13]. The difference in yield of the earlywood and the latewood was attributed to their different chemical compositions. In latewood, the cellulose content is higher and the cellulose had greater resistance to degradative pulping reactions [6]. Xylan reprecipitation was also more evident in latewood than in earlywood [13].

Table 8-5. Properties of Kraft Pulps from Earlywood and Latewood

	Early-1	Late-1	Late-2
H-Factor	1600	1600	2100
Yield, %	45.5	54.4	53.6
Kappa Number	30.1	37.5	28.6
Kappa # after	28.6	36.7	27.5
Extraction			
Extractive Content	0.38%	0.22%	0.19%
Brownstock	28.2	18.3	19.2
Brightness(% ISO)			
Coarseness(mg/m)	0.226 ± 0.012	0.330 ± 0.018	0.318 ± 0.004
Fiber Length(mm)	3.37 ± 0.04	3.63 ± 0.04	3.60 ± 0.02

Under the same pulping conditions, the kappa number of latewood kraft pulps was higher than that of the earlywood kraft pulps. The difference in the delignification rate of earlywood and latewood was mainly due to their different fiber morphology. The cell wall of latewood is much thicker than that of the earlywood. The thick cell wall retards the penetration of cooking liquor, which causes a non-uniform distribution of the cooking chemicals. The surface roughness of earlywood was usually greater than that of the latewood [16]. Besides, the surface tension of earlywood was higher. With this respect, cooking liquid penetration in latewood was much slower. Even a thorough impregnation may result in a drastically uneven distribution of chemicals between earlywood and latewood portions. And, because of the difference in lumen dimensions,

earlywood contained disproportionately more cooking chemicals than latewood [17]. This gave a tendency of overcharging the earlywood and increasing the rate of degradation of lignin and cellulose. Therefore, the pulp from earlywood resulted in lower kappa number and lower yield.

Kraft pulp from earlywood had higher extractive content than that from latewood, as found in earlier studies [6, 13]. The coarseness of the latewood pulp was about 50% higher than that of the earlywood pulp, indicating the much thicker cell wall of the latewood pulp. The fiber length of the latewood pulp was about 10% greater than that of the earlywood pulp, as found in an earlier study [18].

At around the same kappa number, the brightness of latewood unbleached pulp was about 9% ISO lower than that of the earlywood unbleached pulp. According to Kubelka-Munk theory, the sheet brightness is approximately described as

$$R_{\infty} \approx 1 - \sqrt{\frac{2K}{S}}$$

where K is the absorption coefficient and S is the scattering coefficient [19]. K depends primarily on the degree of pulp bleaching. At the same kappa number, the earlywood and latewood fibers have approximately the same K value. The light scattering coefficient S arises from the specific surface area (area per unit mass). Studies found that the light scattering coefficient S of fibers with thinner fiber wall was higher [20]. The light scattering coefficient S of earlywood fibers was high due to its small cell wall thickness [19]. Therefore, at the same kappa number, the brightness of earlywood fiber was higher than that of latewood fibers.

Leaching Properties of Earlywood and Latewood Pulps

Leaching studies measure the rate of bulky lignin diffusion out of the fiber cell wall. The leaching properties of Early-1 and Late-2 are shown in Figure 8-1.

Due to its thicker cell wall, the latewood pulp had a lower leaching rate than the earlywood pulp. The difference in leachability will affect the bleachability of the latewood pulp and the earlywood pulp.

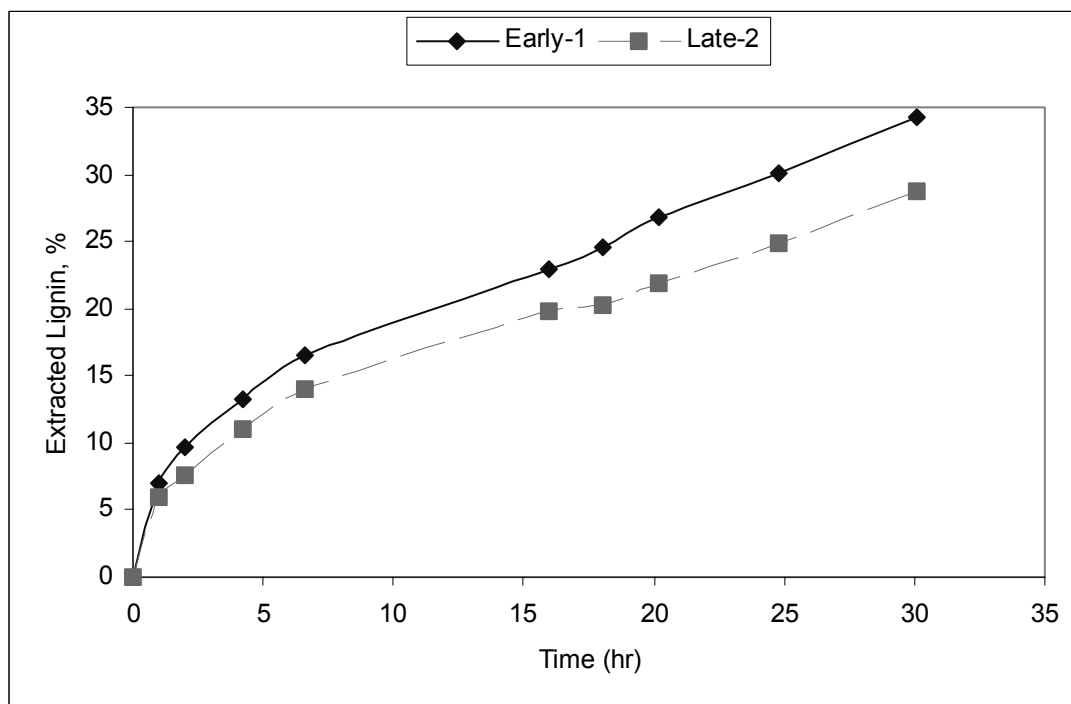


Figure 8-1. Leaching Process of Extractive-Free Pulps

Bleaching Properties of Earlywood and Latewood Pulps

The earlywood and latewood chips were from the same log. Under the same pulping condition and at the same kappa number, the earlywood and latewood pulps would presumably have the same residual lignin structure. The difference between these two pulps was the difference in the extractive content and the fiber coarseness. The brightness of earlywood and latewood pulps without organic solvent extraction is shown in Figure 8-2 and Figure 8-3.

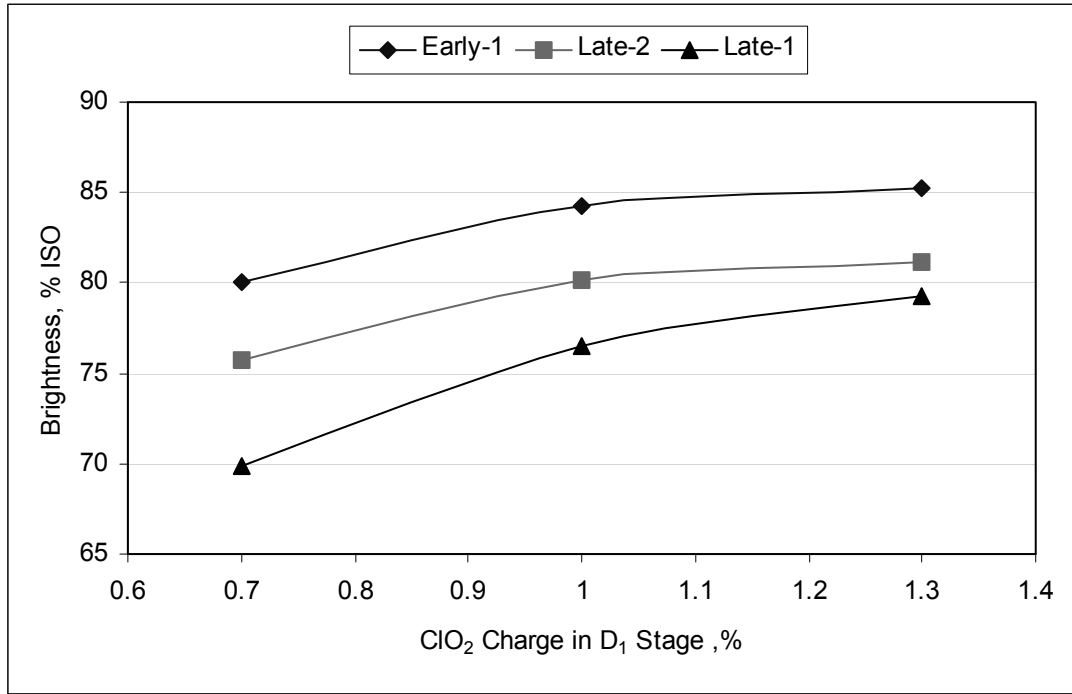


Figure 8-2. Brightness after DEopD

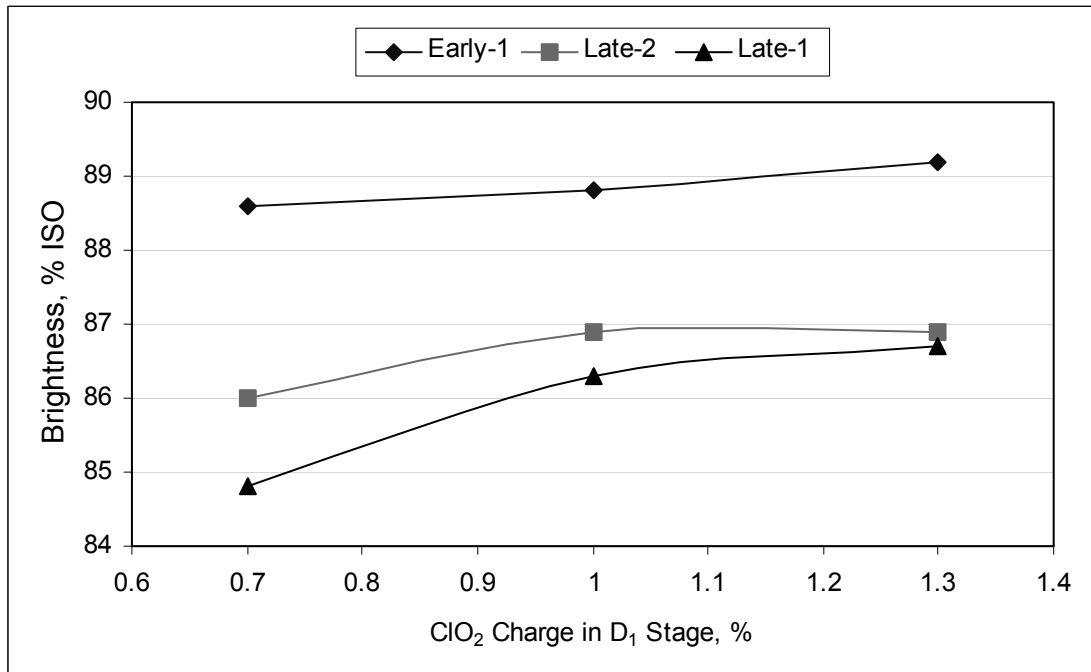


Figure 8-3. Final Brightness after DEopDED

After 3 stages (DEopD) of bleaching, the brightness of earlywood pulp was about 4% ISO higher than that of the latewood pulp. After 5 stages of bleaching, the brightness of earlywood pulp was about 2-3% ISO higher than that of the latewood pulp.

To exclude the difference in the extractive content, all the pulps were extracted with organic solvent before bleaching. Thus, the difference in bleachability of earlywood pulp and latewood pulp came only from the difference in their fiber wall thickness. The brightness of earlywood and latewood pulps after organic solvent extraction is shown in Figure 8-4 and Figure 8-5.

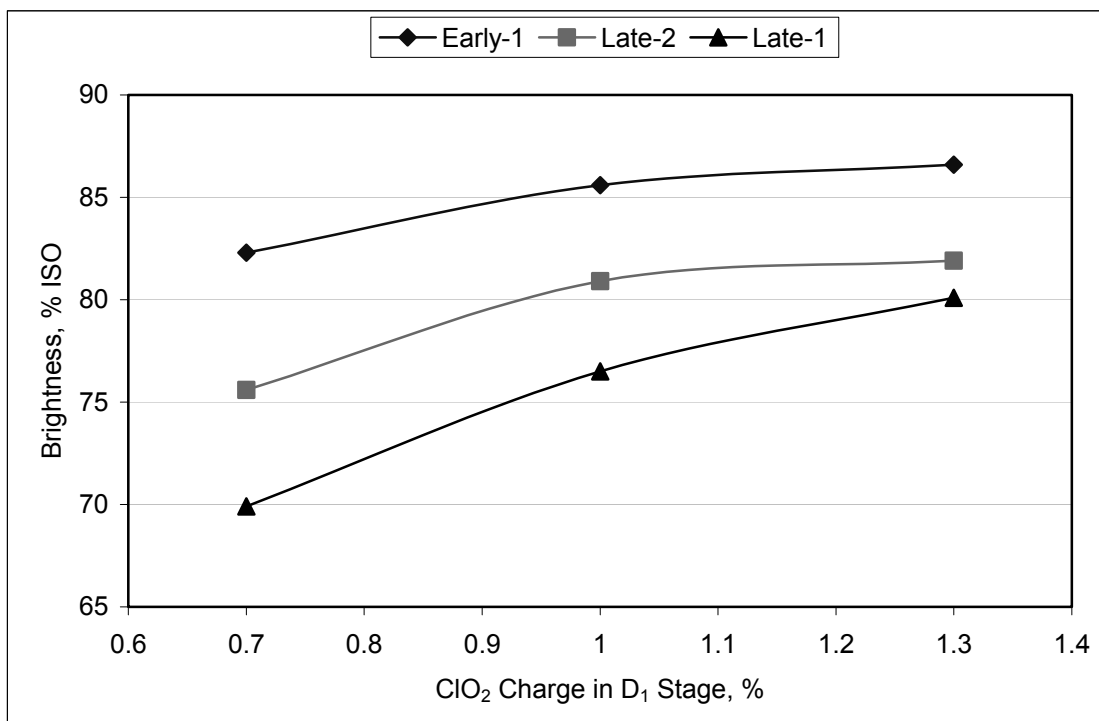


Figure 8-4. Brightness after DEopD

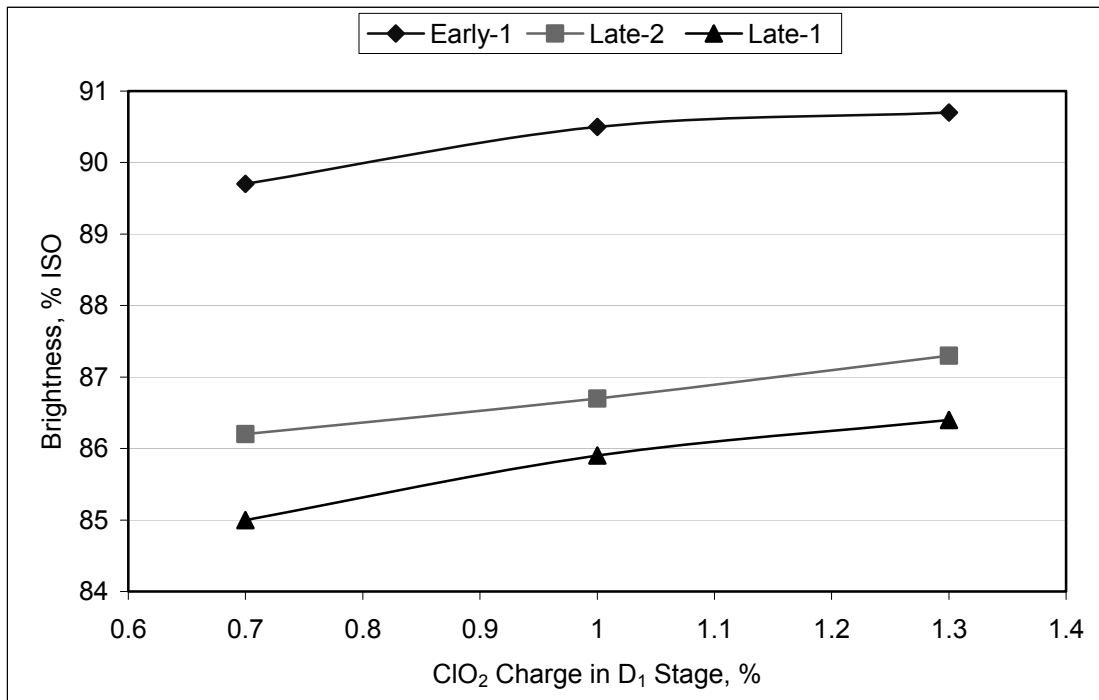


Figure 8-5. Final Brightness after DEopDED

After organic solvent extraction, the final brightness of latewood pulps was about the same. However, the final brightness of earlywood pulps was increased at least by 1% ISO due to its higher extractive content.

In a previous study, it was found that the blocking effect of extractives for the softwood pulp was very dominant due to its thick cell wall [21]. For the latewood pulp from loblolly pine, though its cell wall was about 50% thicker than that of the earlywood pulp, its bleachability was barely improved with the removal of extractives. On the other hand, the bleachability of the earlywood pulp with thinner cell wall was strongly affected by the extractives. This result indicated that the cell wall thickness was the dominant factor in determining the bleachability of earlywood and latewood pulps. Therefore, as one of the variables, cell wall thickness affected the bleachability of the pulps.

Conclusion

Fiber morphology affected the pulping and bleaching properties. For earlywood and latewood from loblolly pine, when they were cooked and bleached under the same conditions:

- The yield was higher for the latewood than for the earlywood.
- The kappa number of the earlywood kraft pulp was lower than that of the latewood kraft pulp.
- The leachability of the kraft earlywood pulp was higher than that of the latewood kraft pulp.
- The bleachability of the earlywood kraft pulp was significantly higher than that of the latewood kraft pulp.

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CHAPTER IX SUMMARY

The conclusions from this dissertation are summarized as following:

The extractives in the southern softwood and the southern hardwood conventional kraft pulps affected the bleachability of the kraft pulps. Extractives influenced the ClO_2 bleaching process by reaction and blocking mechanisms. In softwood kraft pulps, up to 10% of the ClO_2 was consumed by extractives. In hardwood kraft pulps, up to 40% of the ClO_2 was consumed by extractives. Extractives in both softwood and hardwood kraft pulps affected the leaching process by blocking the diffusion of the bleaching chemicals and the residual lignin. In softwood, both the neutral extractive compounds and precipitates during cooking had blocking effects. In hardwood, extractives had relatively small blocking effect due to the thin fiber wall.

In batch extended delignification process, extractives accumulated in the pulps during the black liquor recycling, which affected the bleachability of pulps. The amount of extractives precipitating onto the pulps strongly depended the final pH of the pretreatment black liquor. The operating conditions - sulfidity, alkali charge, pretreatment temperature and wood species, determined the precipitation process. More extractives tended to precipitate with lower alkali charge, higher temperature, higher sulfidity in the pretreatment. For hardwood, larger amount of extractives, especially the neutral extractive content, precipitated onto fibers during black liquor recycling than in softwoods.

It is possible to modify the bleachability and extractive content of batch extended delignified softwood kraft pulps by introducing a gas-off process in the pretreatment. The gas-off process affected the pulp extractive content. The amount of extractive content affected the bleachability of the extended delignified pulps. The conditions of pretreatment in extended delignification, such as gas-off temperature, sulfidity and alkalinity, affected the bleachability of pulps. Low gas-

off temperature and high alkalinity in pretreatments lowered the neutral extractive content and resulted in higher bleachability of pulps. More extractives were removed with gas-off at high temperature than at low temperature and more extractives were removed when pretreated with low alkali charge than with high alkali charge.

It is possible to use high temperature gas-off pretreatments to modify the bleachability and extractive content of batch extended delignified pulps. Presteam, white liquor profiling (WLP) and caustic washing were three efficient methods to enhance the performance of the high temperature gas-off process. For the pretreatment with black liquors, the gas-off process had little influence on the extractive content and bleachability of extended delignified pulps. White liquor profiling to the pretreatment liquor and white liquor profiling to the washing liquor were found to improve the bleachability of these pulps. More extractives were removed when the chips were pretreated with white liquor than with black liquors. More extractives were removed during the first several minutes of releasing. Then, the rate of extractive removal was constant.

For the hardwood, the gas-off pretreatment was also a possible way to lower the extractive content of extended delignified pulps as well as enhance their bleachability. The gas-off process affected the extractive content and bleachability of the pulps. Most of the natural volatile substances in southern red oak were acidic compounds. Most of the volatile neutral compounds were generated by saponification reactions and were only volatile at high temperature. The conditions of pretreatment in extended delignification, such as gas-off temperature, sulfidity, alkalinity and black liquor pretreatment, affected the bleachability of pulps.

Not only the extractive content of the pulp but also the fiber morphology affected the bleaching properties. For earlywood and latewood from the loblolly pine, the earlywood had higher lignin content, higher extractive content, more

condensed lignin structure and thinner fiber wall than that of the latewood. When the earlywood and latewood were cooked and bleached under the same conditions, the yield of latewood was 8% higher than that of earlywood; the kappa number of earlywood pulp was lower than that of latewood pulp; the leachability of earlywood pulp were significantly higher than that of latewood pulp. The final brightness of bleached earlywood pulp was at least 2% ISO higher than that of bleached latewood pulp.

CHAPTER X FUTURE RESEARCH

This dissertation focused on the impact of process conditions on the bleachability. Apart from the operating variables, the chemistry reactions in pulping and bleaching processes are the key to explaining the results. The chemistry structure of the compounds in the condensate, the chemical changes of extractives compounds during high sulfidity and low sulfidity pretreatment, the chemical structure of the extractives that precipitated on the fiber need to be characterized in more detail. The reactivity towards bleaching chemical and the affinity to the fiber surface of the extractive compounds can be somehow explained from their molecular structures.

The properties of pulps are affected to a great extent by the surface properties, including the distribution of extractives on fiber surface. The surface properties of the fiber determine the leachability and hydrophilicity of the pulps, which affect the bleachability. How the pulping processes affect the surface properties of the pulp would be an interesting area for more research.

It has been found that the fiber morphology, i.e., cell wall thickness, affects the bleachability of the pulps. The fiber morphology is determined not only by the natural source of the fiber, but also by the processing. Never-dried fibers may have different morphology from once-dried fibers. Refining affects the fiber morphology of the pulp greatly. Therefore, the morphology and bleachability changes of the pulp after different treatments, such as refining to a certain degree, are worthy of studying in some detail.