

ABSTRACT

SINGH, AJAI. Sulfite treatments in RDH and Kraft pulping (Under the direction of Dr. Hasan Jameel)

This research is divided into two parts. First was sodium sulfite as a treatment agent in RDH and kraft pulping. Second was sodium sulfide as a treatment agent in modified kraft pulping.

RDH cooks were done using air dried Southern Pine chips with the addition of sodium sulfite in different stages. Sodium sulfite charge was kept at 2% and 4% on OD chips. Improvement in yield and bleachability were not as expected, so to better understand the behaviour of sulfite, it was used as a pre-treatment chemical in modified kraft pulping. Sodium sulfite charge was varied upto 9% on OD chips in modified kraft cooks. Sodium sulfite was added in the pre-cooking stage, cooking and post-cooking stage. The sulfite charge was even split up between pre-treatment and post-treatment. Split addition of sodium sulfite gave good yield. Bleachability, however, didn't show the expected results. Results of this study indicated that RDH cooks with 4% sulfite charge in the Hot Black Liquor stage did not show any improvement on yield and bleachability. Split addition (pre-cook and post cook stages) of sulfite charge in the modified kraft cook increased the yield but no improvement in bleachability was seen. 0.1% AQ addition in the modified kraft cook improved the yield, but again no improvement in bleachability was achieved.

Sulfide concentration is a crucial factor in kraft pulping. This study looks into the effects of sulfidity on the yield and kappa number in kraft pulping. Sulfidity was varied from 0-100% in all the stages in a 3-stage modified kraft pulping process. Pre-treatment of chips with sodium sulfide resulted in lower kappa number. Yield was higher for cooks at lower H-Factor. Higher sulfidity in the cooking stage gave higher yield at high H-Factor. The results obtained from the experimental and model data indicated that sodium sulfide treatment in the pre-treatment (pre-cook) stage is the most affective with regards to yield and kappa number. The sulfide concentration in the post-treatment (post-cook) stage had no substantial effect on kappa number and yield.

Sulfite treatments in RDH and Kraft Pulping

by

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I would like to dedicate this dissertation to my parents Mrs. Meena Singh and Dr. I.D.Singh and my wife, Mrs. Pallavi Singh . Their love, support and encouragement was instrumental in bringing me to this point of life.

Biography

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INTRODUCTION

Industrial pulping, that is the large scale production of cellulosic fiber for papermaking in pressurized equipment at high temperature, was introduced in the second half of the nineteenth century, in the period from 1853 to 1884.

Alkaline pulping of plant material had been practiced since long in Asia and had reached Europe via the Arabs after 1000A.D. was the first (1853) to be industrialized in the form of the soda pulping process, i.e. using caustic soda as chemical agent and straw as the raw material. The next process, acid sulfite pulping (first patented by Tilghman in 1866/67) deserves special consideration since it presents a true invention without prior art. Again, sulfur dioxide and its aqueous solutions had been known and used since antiquity, not for pulping but for their properties of disinfectant, food preservatives and bleach. The idea of using sulfur dioxide or metal sulfites as pulping chemicals came to Tilghman in Pennsylvania, and later to Ekman in Sweden indirectly from their application as bleaching agents. Ekman's (1872, Sweden) idea was simply a case of trying bisulfite, which he studied as bleaching chemical, also as cooking chemical. Kellner's invention of acid sulfite pulping occurred at about the same time in a soda mill in Austria, in an even more unpredictable fashion. His technician performing soda pulping experiments in the laboratory took by mistake a bottle from the shelf containing sodium bisulfite and used it for liquor preparation rather than caustic soda.

Of these three originators of the acid sulfite pulping process, Tighman used calcium bisulfite, Ekman used magnesium bisulfite and Kellner used sodium base. Ammonium base was neglected during this initial period. Processes appearing after 1900

used neutral ammonium sulfite. The first suggestion of ammonium bisulfite pulping was patented in the US (Sammet and Merrill, 1912) using gaseous sulfur dioxide, ammonia and steam, but the first clear proposal of the acid ammonium bisulfite process is found in patents granted to Marusawa in 1917 in Japan and the US.

The third major development which took place in this period concerns the kraft (sulfate) process (patented 1884 by Dahl in Germany), where sodium sulfide was added to the caustic soda cook. The result of adding this chemical was better bleachability and less cellulose degradation (higher fiber strength than obtained in the severe caustic soda environment).

The first real sulfite mill was built by Ekman in 1874 using rotary digesters and indirect heat by means of a steam jacket to produce magnesium base sulfite pulp. In 1882, Wheelwright brought the Ekman process to America and built the first sulfite mill in Rhode Island. The Mitscherlich process, using calcium base similar to Tilghman, with indirect heating, was developed in Germany about 1880 and installed soon after in the Fletcher mill at Alpena, Michigan. A calcium base sulfite process in upright digesters with direct steam heating was effected in Austria in 1878 by Ritter-Kellner. It was introduced into Canada by Russell and Riordon, and the first sulfite mill built in 1885 at Merriton, Ontario.

While the kraft process remained virtually unchanged, modifications to the sulfite process, away from the original acid sulfite process and into higher pH levels, began to appear after 1930. The first such process was high yield neutral sulfite pulping, mainly for hardwoods, developed for packaging grade. After 1950, sulfite technology moved into the pH range between acid and neutral with the development of bisulfite high yield

pulps mainly for the newsprint. These advances were a result of the environmental concerns with the use of the traditional calcium base, thus increasing shortage of spruce wood and paper strength demands. The semi-soluble magnesium base were finally introduced on a larger scale, resulting in new processes with recovery of chemicals. In Canada, these processes were expanded in the seventies to ultra high yield bisulfite pulping with yields upto 90%.

Finally, in the late sixties, technological investigations began to open up the remaining area of sulfite pulping in the alkaline field. This led to the development of the alkaline sulfite process which for the first time challenged the position of kraft pulping in the field of highest paper strength, offering at the same time easy bleaching and operation at low inoffensive odor. This was followed in 1978 by a sulfite process at lesser alkalinity but with anthraquinone as pulping catalyst. Pulps produced by this most recent extension of sulfite pulping are better delignified, brighter, less degraded and stronger than kraft pulps. Thus, sulfite process now offered pulping in the entire pH range.

Relative to kraft, sulfite pulp production has been standing still since 1945. At the same time, technological advances in sulfite pulping have been numerous and outstanding, notably in Canada, Scandinavia, and, with the advent of anthraquinone accelerator, also in Japan, Australia and South Africa.

Today, most of the world production of bleached chemical pulp comes from the kraft process. A kappa number of 30-35 for softwoods and 18-20 for hardwoods are achieved by removal of about 90-95% of lignin depending on the wood species and pulping conditions. Removal of the highly modified residual lignin by extending the conventional kraft pulping leads to loss of yield and produces a pulp of poor quality due

to carbohydrate degradation. To preserve the yield and quality of the pulp, a multiple bleaching sequence using chlorine and/or chlorine dioxide is practiced. The amount of chlorinated organic compounds formed in the spent bleach liquor is a function of chlorine consumed by the pulp. These chlorinated compounds may be toxic, mutagenic and carcinogenic. Thus, the driving force for change in pulping and bleaching comes from a combination of quality and environmental concerns. In the last decade, environmental regulations have been focused on the reduction or elimination of chlorine and its derivatives from bleaching operations by alternative bleaching agents and other pulping methods. One of these methods is to use extended delignification technologies.

Extended delignification technology enhances the selectivity in the digester by removal of additional amounts of lignin without decreasing yield. The four basic principles of extended delignification proposed by Johansson et al are:

- a) Levelling out of alkali concentration.
- b) Having the HS concentration high at the start of the cook.
- c) To keep the dissolved lignin and Sodium concentration low towards the end of the cook.
- d) To keep the temperature low, especially at the beginning and end of pulping.

Leveling out the alkali concentration at the beginning creates a harsh environment for carbohydrates. A high HS induces a faster and more complete lignin breakdown during bulk delignification. When some lignin already in the solution is removed from the pulping environment, further delignification and diffusion of lignin from the fibers can occur. A lower temperature of pulping improves the selectivity for delignification over

polysaccharides' depolymerization. These approaches allow low kappa pulps going to the bleach plant with comparable yield and pulp qualities.

Currently there are four marketed systems for extended delignification. Of these two operate in the batch mode (RDH from Beloit, Superbatch from Sunds Defibrator), and two use the continuous mode (EMCC from Kamyr, Kavaerner). The batch systems utilize displacement concepts for pre-treatment with black liquor before digestion with white liquor. The requirement for initial high sulfide concentration is accomplished by using the spent cooking liquor with high sulfidity for pretreatment. Displacing the second pre-treatment liquor with white liquor also removes some of the dissolved lignin in the digested medium. The lowering of the cooking temperature will require longer cooking time to reach specific kappa number.

The continuous systems split the total white liquor into 3 or 4 parts and add them at different locations of the process. With countercurrent cooking zone and extraction screens, dissolved lignin and inorganic constituents exit with the black liquor. Below the extraction screens, further delignification occurs and more solubilized lignin can diffuse out of the fiber wall. The lower maximum temperature criterion is met by converting the wash zone into a low temperature cooking zone allowing a longer cooking time.

Pre-treatment of the chips using black liquor before digesting with the white liquor allows a significant reduction of H-factor to reach the same kappa level as in the conventional batch system. Pu et al concluded that depletion of alkali during the pre-treatment stages results in lignin deposition or condensation that is difficult to remove later in pulping.

A disadvantage with the extended delignification process is a yield loss at a kappa of 18-20 for softwoods. This will cause an increase in load going to the recovery. However, use of yield enhancing additives retains more hemicelluloses and increases the pulp yield at a given kappa number. Various additives have been researched, and the most important among them are anthraquinone (AQ), Polysulfide (PS) and Sodium Sulfite (Na_2SO_3). It has been found that with these additives, the kappa number can be reduced without a yield loss. The addition of AQ even in small amounts results in carbohydrate stabilization by the oxidation of the reducing end groups to aldonic acids. AQ in turn is reduced to anthrahydroquinone (AHQ). AHQ acts similar to hydrosulfide towards the cleavage of phenolic beta-aryl ether bonds in lignin and hence, enhanced delignification.

The purpose of this study is to explore the effects of using sodium sulfite in the pre-treatment stages of RDH and kraft pulping on yield, residual lignin and blechability. The lower kappa numbers will help decrease the amount of chemicals used in the bleach plant and reduce the effluents discharged into the environment from the mill.

CHAPTER 1

Chemistry of Kraft Pulping

The kraft process with its application to all wood species and its insensitivity to variations in wood properties makes it the dominant process for the production of chemical pulps in the world. The main task in chemical pulping is the dissolution of lignin and subsequent separation of fibers in the wood. The active chemical agents in the kraft process are hydroxide ions (OH^-) and hydrosulfide ions (HS^-). Hardwood and softwood species vary in the amount of cellulose, hemicellulose, lignin and extractives. The average composition values for softwoods and hardwoods are as follows.

	Softwoods	Hardwoods
Cellulose	42	45
Hemicellulose	27	30
Lignin	28	20
Extractives	3	5

Kraft pulping enables lignin to be released by the delignification reactions between hydroxide ions, hydrogen sulfide ions and lignin. Since the cooking liquor is not totally selective for lignin, the cooking liquor (primarily hydroxide ions) also degrades carbohydrates. This degradation of carbohydrates results in the loss of yield and strength.

1.1. Carbohydrate Reactions

The degradation of carbohydrates in alkaline pulping lowers the yield and results in a weak pulp. The extent to which the carbohydrates undergo degradation and dissolution in the hot alkaline cooking liquor is governed by the degree of crystallinity or accessibility, position, abundance of side branches on the backbone chain (in hemicellulose only), extent of delignification, initial and final pH of the liquor and the presence of stabilizing additives. Cellulose and hemicellulose, are collectively known as Holocellulose. Cellulose is a linear, partially crystalline polymer of anhydrous glucose with a degree of polymerization (DP) of approximately 10,000 units. Hemicellulose is an amorphous co-polymer of two or more sugars with a DP of 120-200 units.

Two main types of hemicelluloses are xylans and glucomannans. During the early stages of the cook, acetyl groups of hardwood xylans and softwood glucomannans are hydrolyzed. The degradation of polysaccharides leads to the formation of a hydroxy acid for every monosaccharide removed. The degradation is due to the reactions with hydroxide anions and is independent of sulfide or hydrosulfide anion concentration. Conventional alkaline pulping of softwood results in the loss of about 10-15% cellulose, 80% or more of glucomannan and 20-50% of the xylan along with the removal of 90-95% lignin.

The two main reactions in alkaline pulping responsible for carbohydrate degradation are:

1. Stepwise depolymerization (peeling reaction)
2. Random hydrolysis.

1.1.1. Stepwise Depolymerization

Peeling reaction is base catalyzed and occurs at relatively low temperatures. Hemicelluloses degrade more extensively because of their low degree of polymerization and their amorphous state. The terminal aldose unit also known as reducing end group (REG) in the polysaccharide chain is removed causing isosaccharinic acid to be produced with a new REG for further alkali attack as shown in Figure I. An average of 60-65 of these monomers are cleaved before a slow competing "Stopping reaction" as shown in Figure II converts the REG's to an alkali stable acid end group. Base catalyzed enolization of the aldehyde group, the Lobry de Bruyn-Alberda van Ekenstein rearrangement, is the first step in both the peeling and stopping reactions. The fructose end unit in its enol form (2,3-dienol) is subject to β -glycosyl elimination, exposing a new reducing end group and thus leading to a stepwise depolymerization (peeling) of the polysaccharide chain.

The peeled unit undergoes a special carbon-carbon bond cleavage known as Benzil-Benzilic acid rearrangement in alkali, resulting in the formation of an isosaccharinic acid. Further rearrangement and another benzil-benzilic acid rearrangement generates a metasaccharinic acid end group on the polysaccharide chain, thus stopping the reaction. 60-70% of the alkali is consumed for the neutralization of the acids formed from the peeling reaction. The remaining alkali is used to neutralize uronic and acetic acids, and for delignification.

1.1.2. Random Hydrolysis

Random hydrolysis sets in at temperatures higher than 140°C producing new reducing end groups which leads to further peeling reactions known as “secondary peeling”. At temperatures greater than 140°C, the glycosidic chain rearranges into the boat conformational isomer, as shown as in Figure III, and leads to random hydrolysis which allows backside attack to occur. The β -1, 4 linked polysaccharide is involved in an internal nucleophilic substitution reaction, which eventually causes the C-2 hydroxyl group to be ionized. Random hydrolysis and secondary peeling are damaging to the average chain length, and decrease the pulp strength and viscosity. The pulp yield is adversely affected because the cleavage generates a new REG, subject to “secondary peeling” at the higher temperatures. Lactic and formic acids are formed by further complex fragmentation reactions that occur at higher temperatures.

1.2. Lignin Reactions

Lignin is a three-dimensional, polydisperse, cross-linked polymer composed of phenyl propane units. Figure IV shows the different types of bonds interconnecting the units. In kraft pulping, the delignification is divided into three phases, namely the initial, bulk and residual, as shown in Figure V. The delignification can be considered first order with respect to the lignin remaining if the liquor concentration is kept constant during pulping. The initial phase occurs between 70-140°C temperatures and is controlled by diffusion. Pekkala reported initial delignification easily removes about 20-25% of lignin. The dissolution of lignin in this stage is assumed to be caused by the cleavage of α -aryl

and α -aryl ether bonds. The cleavage of non-phenolic β -aryl bonds in lignin results in maximum removal of lignin in the bulk delignification stage. Efficient cleavage of ether structures therefore constitutes one of the most important reactions in alkaline pulping. 80-90% of the lignin is removed in the heat up stage (time to temperature) from 140-170°C and at 170°C (time at temperature). The delignification rate increases with an increase in temperature in this phase. In the residual stage, only 10-15% of native lignin is removed along with extensive dissolution of carbohydrates. The delignification rate is very slow due to the depletion of the chemicals, as well as due to the fact that residual lignin has many bonds that are difficult to cleave by hydrolytic processes. This non-selective residual phase limits the conventional kraft process delignification to about 30-35 kappa number.

1.2.1. Lignin structure and bonds

Several types of chemical reactions take place during alkaline pulping that affect the structure of the lignin remaining in the fibers at the end of the process. Kraft pulping involves the cleavage of ether linkages and their dissolution in the cooking liquor. Experiments with model compounds have helped to understand the reactions occurring during delignification in the lignin structure. In the following sections, the reactions and process parameters that are believed to have a major impact on structural characteristics of lignin are reviewed.

1.2.1.1. Alpha-aryl Ether bonds

These appear in both phenolic and non-phenolic structures. Non-phenolic alpha-ethers however, are easily cleaved during the initial, low temperature phase of cooking as shown in Figure VI. They generate a quinone methide structure with a new phenolic hydroxy group which then gives a stilbene structure with the elimination of a proton from the beta position. These reactions can and do occur in the initial phase of delignification, affecting only lignin units possessing a free phenolic hydroxyl group.

1.2.1.2. Phenolic Beta-aryl Ether bonds

The Beta-aryl ether bonds appear as phenolic and non-phenolic. These account for about half of the total lignin linkages. Hydrolytic splitting of this bond is the most important fragmentation reaction in the alkaline delignification process. The quinone methide intermediate shown in Figure VII, is formed with the removal of hydroxy or aryl group from the α carbon. This is considered as the rate determining step of the overall reaction. The strong nucleophile, HS^- anion is then added to the quinone methide giving the benzyl mercaptide structure, which then attacks the β carbon atom forming thirane intermediates with elimination of β -aryl ether bond. P-hydroxystyrene structures are formed by the elimination of sulfur from thirane. Elemental sulfur combines with hydrosulfide to form polysulfide.

1.2.1.3. Non-Phenolic Beta-aryl Ether bonds

Hydrolytic cleavage of β -aryl ether bonds in non-phenolic units requires the participation of a neighbouring ionized group. This group must be present on the α or γ -carbon of the side chain. This type of β -aryl ether linkages in non-phenolic structures, as

shown in Figure VIII, is cleaved very slowly in the bulk phase, and it is the rate determining step of the lignin dissolution in this phase. This is the dominant type of splitting in the soda process. This cleavage liberates new phenolic structures which is the starting point for cleavage of phenolic α -aryl and β -aryl ether bonds.

1.2.1.4 Cleavage of Carbon-Carbon bonds

This is considered as a minor reaction in lignin fragmentation as these bonds are more stable than ether bonds under hydrolytic conditions. The splitting of C-C bonds mainly occurs by reverse aldol reactions. The bond cleavage is greatly facilitated by :

- a) Factors favoring the dissociation of the OH⁻ group on the α -carbon, such as high pH and high temperature.
- b) Presence of electron withdrawing groups on the β -carbon, such as CHO, COOH, NO₂ and CN.

1.2.1.5. Condensation Reactions

The alkaline conditions prevailing in kraft pulping favor a variety of condensation reactions between lignin units and carbohydrates. The alkali concentration decreases at the end of the cook resulting in the undesirable lignin condensation reactions. These reactions result in new alkaline stable carbon-carbon bonds that increase the size of the lignin fragments, thereby reducing their solubility in the kraft liquor. The re-deposition of the dissolved lignin on the pulp occurs. Four main modes of lignin-lignin condensation reactions have been identified on the basis of medel compounds. The two general condensation reactions that take place during the cook are given in Figure IX.

Nucleophilic addition of various carbanions to a quinone methide is also known as condensation reaction. The primary condensation reaction involves the quinone methide formed when the alpha substituent is eliminated. The extended quinone methide formed from conjugated phenolic structures that are generated after the initial ether cleavage reactions give secondary condensation. The presence of a strong nucleophile or high alkalinity, which compete with the carbanions, suppresses these undesirable reactions.

Chapter 2

Chemistry of Sulfite Pulping

2.1 Lignin

Of interest here is the interaction between sulfur dioxide in water and lignin. According to an early theory, the process of dissolving lignin is separated into two steps:

1. The lignin in the solid phase is sulfonated.
2. Lignin dissolves by hydrolysis under the catalytic action of hydrogen ions.

According to this theory the degree of delignification is proportional to the acid concentration and depends on the presence of cations other than hydrogen ions. Hydrolyzed lignosulfonic acid is then sulfonated further in the solution.

According to other authors, the degree of delignification is proportional to both the concentration of acid and the concentration of bisulphite ions. According to this concept, sulfonation of the lignin is the rate determining step rather than hydrolysis of the lignosulfonic acid formed.

Part of the Kalson theory is the addition of sulfur dioxide to an ethylene bond in the lignin molecule. However, the existence of ethylene double bonds in lignin molecules could not be verified. Freudenberg and co-workers proposed that sulfur dioxide combines in two steps:

1. The opening of a pyran or furan ring.
2. The formation of a secondary phenolic hydroxyl.

The latter is partly replaced by $\text{SO}_3^+ \text{H}^-$, directly or after the release of water. On the other hand, recent investigations have shown that the ultraviolet absorption of lignin is not influenced by sulfonation, suggesting that sulfonation cannot be considered a reaction with an unsaturated system. It was assumed, then, that sulfonation occurs at an alcoholic hydroxyl group or at a carbonyl group in the propane chain of the lignin molecule. When wood is heated with bisulfite cooking acid, a “solid”, insoluble lignosulfonic acid is formed at first. This functions as a cation exchanger and absorbs calcium ions from the acid, increasing the acidity of the latter. Sulfonation then enters the second stage, leading to the solubilization of the solid lignosulfonic acid. The cation exchange capacity of sulfite pulp is due to the presence of solid lignosulfonic acid.

At high concentrations of total sulfur dioxide, the rate of dissolution of the lignin depends exclusively on hydrolysis whereas at lower concentration of total sulfur dioxide, the rate is also influenced by the sulfonation reaction. The degree of sulfonation depends also to a large degree on the temperature. At low temperatures, sulfonation requires periods of several months, the presence of combined sulphur dioxide being detrimental in this case. After wood prehydrolysis, both sulfonation and subsequent dissolution of the sulfonated lignin is inhibited.

It was found that the amount of sulfur exchanged between bisulfite solution and the sulfonated lignin increased during the first hour until a constant level was reached.

No direct relation was observed between the amount of sulfur exchange and the original sulfur content of the lignin sulfonate. A linear relation was found, however, between the time necessary for the dissolution of a certain fraction of lignin sulfonate and its original sulfur content.

Lignin-sulfonates obtained from hemlock, spruce and maple by treatment with acid bisulfite solutions were investigated as to their average molecular weight. Lignin sulfonates from gymnosperms show initially a low molecular weight followed by a maximum, a minimum and a final rise. Among the bonds between lignin building units, one type can be hydrolyzed easily in acid solution, the other can not. When the bonds between building units are destroyed by sulfonation and hydrolysis of the sulfonate, only soluble portions of low molecular weight diffuse at first while the higher molecular portions follow only at an advance degree of delignification. As the hydrolysis of the dissolved lignosulphonates proceeds, portions of higher molecular weight accumulate and cause the molecular weight to reach a maximum towards the end of lignification. When all hydrolyzable bonds are cleaved, the average molecular weight reaches a minimum and this is finally followed by a rise in molecular weight due to condensation reactions. When hemlock is delignified with acid sodium bisulfite solutions of increasing acidity (pH 4.8 – pH 2.1), one third of the lignin can be removed under weak acid conditions. Lignin sulfonates prepared in this manner have an average molecular weight of 3000. More highly acidic solutions are required to remove remaining portions of the lignin whose average molecular weights are in the order of 30, 000. During subsequent hydrolysis, the molecular weight decreases noticeably, but only to a certain minimum

value. A further decrease in molecular weight is probably counteracted by condensation reactions.

Some studies show that the dissolution after sulfonation might be a mixture of two reactions, hydrolysis and sulfitolysis. According to this hypothesis, the primary reaction is in both cases a proton addition to an oxygen atom of the benzene ether and cleavage of the C-O bond. Then the sulfonate is due to sulfitolysis and the total delignification process can be considered as a one-stage process where solution occurs at a certain degree of sulfitation.

It has been demonstrated that it is possible to delignify with sulfur dioxide solutions without a base. Among others, mixtures of aqueous sulfur dioxide with methanol and other water-soluble organic solvents have been employed. This reduces the lignin condensation to a large extent. When sulfonation is carried out at high sulfur dioxide concentrations and low temperatures, the danger of lignin condensation can be largely avoided even in the absence of organic solvents. The subsequent hydrolysis of lignosulfonates is carried out at temperatures much above those normally used in sulfite cooking. Addition of sodium sulfate to sulfur dioxide solutions results in reaction conditions similar to normal sulfite cooking with respect to bisulfite and hydrogen ion concentration.

2.2. Cellulose

The process of degrading cellulose down to glucose is influenced by temperature and concentration used. The action of sulfur dioxide in water as a hydrolytic agent has been elaborated. By contrast, the purpose of the sulfite cooking process is to safeguard carbohydrates.

During the sulfite cook, long cellulose chains are split into shorter fractions. A slow indirect cook lowers the degree of polymerization (DP) to 1900-2000 whereas a rapid direct cook may cause the DP to drop to 1400. Hence, the sulfite pulping process is responsible for a certain uniformity as far as chain length differences are concerned.

In order to increase the rate of the cooking process it has often been suggested to have some mechanical action on the digester charge during the cook. Such practices, however, cause considerable damage to the cellulose. However, when such mechanical treatment was applied during sulfite cooking in an inert atmosphere, the resulting fiber damage was relatively small. Small amounts of oxygen were, therefore, held responsible for exerting a large effect on the hydrolysis reaction. There is no doubt that lignin plays a protective role and that the danger of damaging the cellulose by hydrolysis increases with progressive delignification. Hardwood cellulose is considerably less protected by lignin and very mild cooking conditions are required.

As seen in Figure X, cellulose shows the least resistance against degradation at pH 7. It shows a maximum of resistance, however, in very acid region and another maximum near pH 11.

2.3. Hemicellulose

During the sulfite cooking process, the sulfur dioxide solution reacts not only with lignin and cellulose but to a certain extent also with hemicellulose and other low molecular fractions and decomposition products originating from cellulose. On the average the following amounts of hemicelluloses are present in the sulfite cooking acid from a spruce cook :

Arabinose	34.3%
Xylose	25.5%
Galactose	9.2%
Mannose	26.5%
Glucose	4.4%

Pulps having a low content of alkali resistant cellulose are usually lower in xylan and higher in glucomannan. Glucomannans show a higher resistance to the hydrolytic action in a sulfite cook than against the alkaline conditions in the kraft cook. The 4-O-methylglucurono-araboxylans of softwoods are converted into 4-O-methylglucurono-xylans whereas those present in the hardwoods suffer a great reduction in their DP. A large portion of these low molecular fragments goes into the solution and only a small portion remains associated with the cellulose. Other hemicellulose fractions of lesser importance in softwoods, such as arabo-galactan, galacto-glucomannan, pectin and starch are less stable against hydrolysis and hardly survive the process. The best explanation of the difference between specific properties of sulfite and kraft pulps are found in the difference of their resistance to acid and alkaline hydrolysis.

If sulfite cooking is preceded by an extended impregnation period, the resistance of the glucomannan of softwoods to the hydrolyzing effects of the cooking acid is increased. It is assumed that glucomannan fragments are associated with wood cellulose by absorption. Polysaccharides which are dissolved during the impregnation and are further degraded in the course of the cook may have a significant effect on the properties of pulp if re-adsorbed by the fibers. Sulfite cooking acid during impregnation of a spruce cook at 110°C had the following composition when examined by paper chromatograph :

Galactose	20.8%
Glucose	15.8%
Mannose	59.3%
Xylose	4.1%

4-O-methylglucurono-arabinoxylan very rapidly loses arabinose units and is degraded under acid cooking conditions. In the homogeneous phase, the content of glucuronic acid in an acid cook remains nearly constant, but it is found to be decreased in a xylan isolated from a pulp cooked at pH 3. Under similar conditions glucomannan is found much more resistant than glucurono-arabinoxylan.

A study of the formation of aldonic acid during sulfite cooking has shown that arabonic acid appears in solution at an early stage. Xylonic acid makes its appearance also very early. The concentration increases gradually as the cook proceeds and approaches a constant value at the end. Manonic acid is present only in small amounts at

the beginning but exceeds the other aldonic acids at the end of the cook. At a pulp yield of about 40%, 50% of the arabinose units, 9% of the manose units and 15% of the xylose units are converted into the corresponding aldonic acids.

Figure XI shows the relationship between the hemicellulose content in the cooking acid and cooking time. This illustrates quite clearly the increase in the hemicellulose concentration during the impregnation period and in the temperature interval 100-110°C followed by rapid decrease as the temperature rises further. Figure XII shows the hemicellulose content of the pulp in relation to the pH value during the cook.

Increase in temperature from 125°C to 160°C in a 2-stage sulfite cooking process will move the pH effect approximately 1.5pH units towards more acidic conditions. The effects of de-acetylation, pulp yield improvement and increase in glucomannan content of the pulps are occurring in parallel in this 2-stage process. The hydrolytic resistance of glucomannan in pretreated holocellulose was found to show the same dependence on pH and temperature as did the wood pulping reactions.

Two-stage pulping of birch resulted in a two to three percent higher pulp yield compared with conventional acid sulfite cooking. The removal of the acetyl groups from the xylan does not indicate that xylan is fractionated during cooking with respect to its uronic acid content.

Chapter 3

Extended Delignification

The beneficial impact on the environment is the primary driving force for extending delignification in the digester. In conventional cooks delignification below 30 kappa number results in lower pulp yields. The remaining lignin is removed by various bleaching sequences that typically use chlorine compounds and caustic extractions. The chlorine based chemicals in mill effluents may produce toxic and carcinogenic substances that are environmental hazards. Maximum removal of lignin prior to the bleach plant lowers chemical costs, provides easier bleachability and reduces toxic effluent discharge into the environment. Since the organics in the spent pulping liquors are generally burnt in the recovery boiler, there will be less organic substances in the discharge.

Extended delignification is the name given to the process of producing pulps at low kappa numbers by modification to the kraft cooking system without severe pulp yield and strength loss. To accomplish extended cooking and maintain pulp strength, several criteria apply.

- 1) Cooking must be uniform throughout the digester
- 2) Cooking must be uniform throughout each wood chip's cross-section.
- 3) The cooking chemistry should be modified appropriately.
- 4) High pulp strength must be ensured.

For good results it is important to fulfill as many of these criteria as possible. Well-controlled displacements aim at uniform distribution of chemicals and heat. Due to high initial temperature after the hot cooking liquor displacements, liquor circulation time during cooking is reduced. The high liquor to wood ratio facilitates rapid liquor penetration, and the role of digester circulation changes from heat transfer to mass transfer, acting as a smoothening aid to achieve a uniform degree of delignification. The cooking liquor chemicals penetrate uniformly and deeper into the wood chips in displacement batch cooking than in conventional kraft cooks. Successive liquor displacements neutralize and remove wood acidity and make it easier for the liquor to penetrate the chips deeper. With low initial treatment temperatures and a fast rate of rise to cooking temperature with the white liquor, a short and uniform cooking phase is accomplished. Chip thickness, depth of delignification and inside digester non-uniformity can be obstacles for lower kappa numbers in extended delignification. With this, the amount of uncooked or very high kappa material will be greatly reduced leading to low rejects. The modified cooking chemistry is proposed to solve the loss of yield resulting from extending the conventional cooks. The chemical modifications to conventional cooks fall into the following categories:

- 1) Pre-treatments (such as Sodium Sulfite)
- 2) Cooking additives (such as AQ)
- 3) Profiling OH^- and HS^- concentrations.

Another important consideration for extending the delignification is the application of the modification. The two considerations are:

- 1) Front end modifications
- 2) Back end modifications

Previous studies show that the hydroxide effect during pulping is divided into four distinct phases:

1. Initial
2. Transitional
3. Bulk
4. Final

An increase in hydroxide concentration during any of the four phases results in the decrease in pulp strength. This is due to an increased rate of random hydrolysis induced by higher hydroxide ion concentration. In conventional cooks, high alkali at the beginning of the cook creates a harsh environment and leads to degradation of carbohydrates. The degraded carbohydrates form organic acids, which consume additional alkali. This leads to reduced alkali in the cook and conditions favorable for lignin condensation. In modified cooking, this situation is prevented by having low alkali at the beginning of the cook which prevents excessive carbohydrate degradation by peeling reaction.

The initial phase delignification is of zero order with respect to sulfide concentration. In chips pretreated with a sulfide containing solution, the bulk delignification proceeds faster. The sulfur in the lignin molecule induces increased lignin solubility when exposed to strong alkali solution. Pre-treatment of chips with spent

cooking liquor containing high sulfide concentrations meets the requirement for initial high sulfide liquors. It has been observed that the presence of lignin from the previous cook also increased the bulk delignification rate which resulted in a higher viscosity at a given kappa number. If sufficient hydrosulfide is present during the bulk phase, the delignification rate increases. An increase in the hydrosulfide ion concentration during the bulk phase also leads to a reduction in residual lignin. The pulp viscosity decreases as the hydrosulfide ion concentration is lowered in the transitional and bulk phases of delignification. This is due to the formation of thirane ring that cleaves the β ether bond in lignin.

Removal of dissolved organic solids in the cooking liquor is another requirement for extended delignification. Basket pulps removed without blowing show an inherent advantage in strength properties over traditionally blown cooks. This is due to the elimination of mechanical force that affects the fibers when blown from the digesters at high temperatures and pressures. Displacement of the treatment liquors with the white cooking liquor reduces the dissolved lignin in the digester. This is dependent on the amount of white liquor injected for cooking. At the end of the cook, lignin condensation is prevented by sufficient hydroxide ion concentration present. The selectivity of delignification is improved by pulping at lower cooking temperatures. Lower cooking temperatures favor better delignification over polysaccharide depolymerization, however, lowering the cooking temperatures leads to longer cooking times to reach a target kappa number.

3.1. Rapid Displacement Heating (RDH) kraft pulping

This process was first introduced by Beloit Corporation as a new batch cooking process in 1984. Its advantages are as follows:

- 1) Digester steam savings
- 2) Extended delignification
- 3) Improved pulp strength
- 4) Lower bleaching cost
- 5) Lower effluent and environmental loads

RDH is a modified kraft cooking process that involves pre-treatment with warm and hot black liquors to save energy and promote extended delignification. The warm and hot black liquors are made up of spent cooking liquors that are recycled from the previous cook. The RDH cycle, as shown in Figure XIII, begins with the chips being steam packed in a hydraulically full digester by pumping in an excess amount of warm black liquor (WBL) till it overflows. The overflow liquor is sent to the evaporators for recovery of heat and cooking chemicals. The WBL is next displaced by hot black liquor (HBL) at approximately 155°C temperature. The displaced liquor is sent to the WBL storage tank with any excess HBL going to the evaporators for recovery. White liquor (WL) is then pumped into the digester displacing the HBL. The displaced liquor is sent to the HBL and WBL storage tanks. H-factor calculations begin with the introduction of WL and the digester is brought to its final cooking temperature of 170°C. When the desired H-factor is reached the now spent liquor is displaced by the wash filtrate (WF) to lower the

digester temperature and also to wash the chips. The washed chips are further washed in the brownstock washers.

The objective of extended delignifications is to maintain a constant level of OH concentration in the cook. The effective alkali of WBL and HBL are ~10 g/L and ~18g/L, respectively. The effective alkali starts at a low level and is progressively raised as the cook proceeds. Maintaining a high concentration of HS ion concentrations improves the selectivity and delignification. To facilitate cold blow, the WF is used to displace the cooking liquor and the pulp is removed by a pump or by blowing with compressed air. This prevents mechanical damage to the fiber.

3.2 Pre-treatment in RDH pulping

Pre-treatment before actual kraft cooking produces more homogenous pulping that reduces the amount of rejects and improves the pulp strength. Recycling of the spent liquor for chips pre-treatment saves energy and time required to reach a target kappa number. The RDH cook has an initial concentration of free hydrosulfide ions which is about four time higher than in a conventional kraft batch cook of same sulfidity. The saturation of lignin with residual sulfur in the spent liquor makes the lignin in the wood chips more vulnerable and is selectively degraded in the cooking stage. The dissolved extractives act as surfactants and improve contact between lignin and the cooking chemicals and facilitate the dissolution of lignin. The spent liquor from the end of cooking stage is first displaced into the HBL tank and then into the WBL tank, to be used in the next cook. The pre-treatment liquor concentrations fluctuate with the white liquor

alkali charge. Several transition cooks at each active alkali charge eliminate these fluctuations of pre-treatment liquor concentrations. Using high active alkali charges of pre-treatment liquor results in faster dissolution of easily removable lignin and carbohydrate fractions of the wood. Reduction in the kappa number reaching the bleach plant substantially reduces the amount of chemicals used in bleaching. Termination of HBL pre-treatment stage with displacement of HBL liquor and injection of white liquor lowers the concentration of dissolved organics prior to attaining cooking temperatures.

Abuhasan concluded that the strengths of the pre-treatment liquor's effective alkali in WBL and HBL has a strong influence on the final kappa number at a constant H-factor and alkali charge. The alkali consumption during pre-treatment for dissolution of hemicelluloses and lignin has a direct impact on pulping response in the final cooking stage. The variation in time and strength of alkali in the warm black liquor stage influences the final pulp yield and kappa number. A higher pre-treatment temperature leads to more degradation of easily removed lignin and carbohydrates before the cooking stage. Too short a pre-treatment in the WBL stage results in greater alkali consumption in the subsequent stages and a higher kappa number pulp. About 40% of the hemicellulose is removed during the WBL treatment. Prolonging the WBL treatment will result in even greater delignification rate and the loss of yield is directly proportional to the time of pre-treatment. Increasing the WBL strength also resulted in greater delignification. Maintaining a consistent pre-treatment temperature during each pre-treatment stage ensures less variation in pulping responses for a given H-factor and alkali charge.

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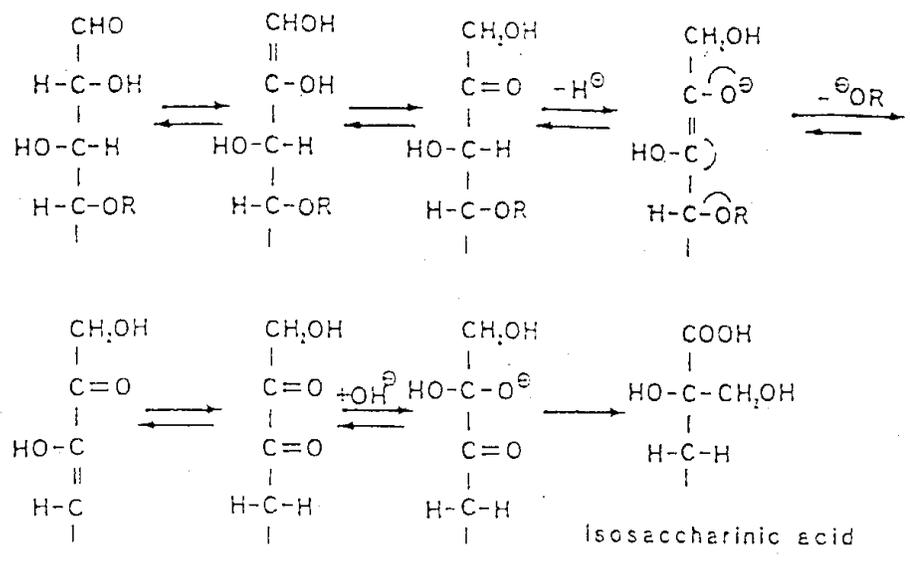


Figure I – Peeling Reaction in alkaline pulping

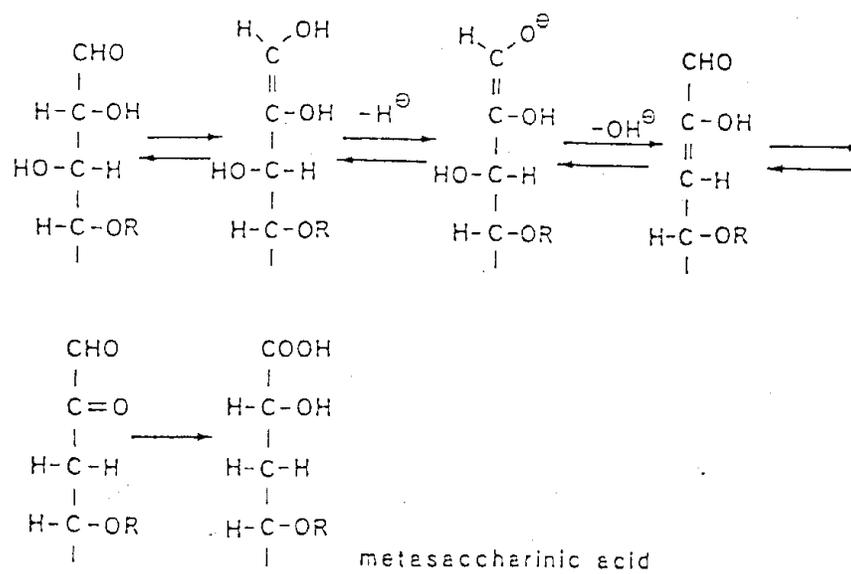


Figure II - Stopping Reaction in alkaline pulping

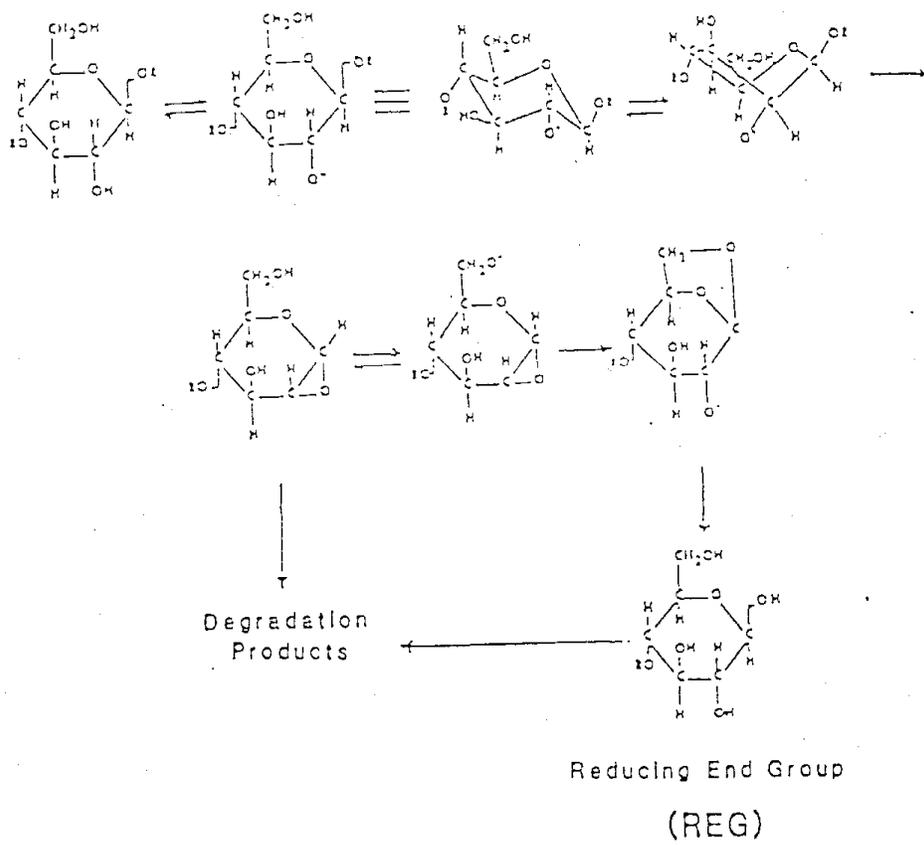


Figure III - Random hydrolysis of glucosidic bonds

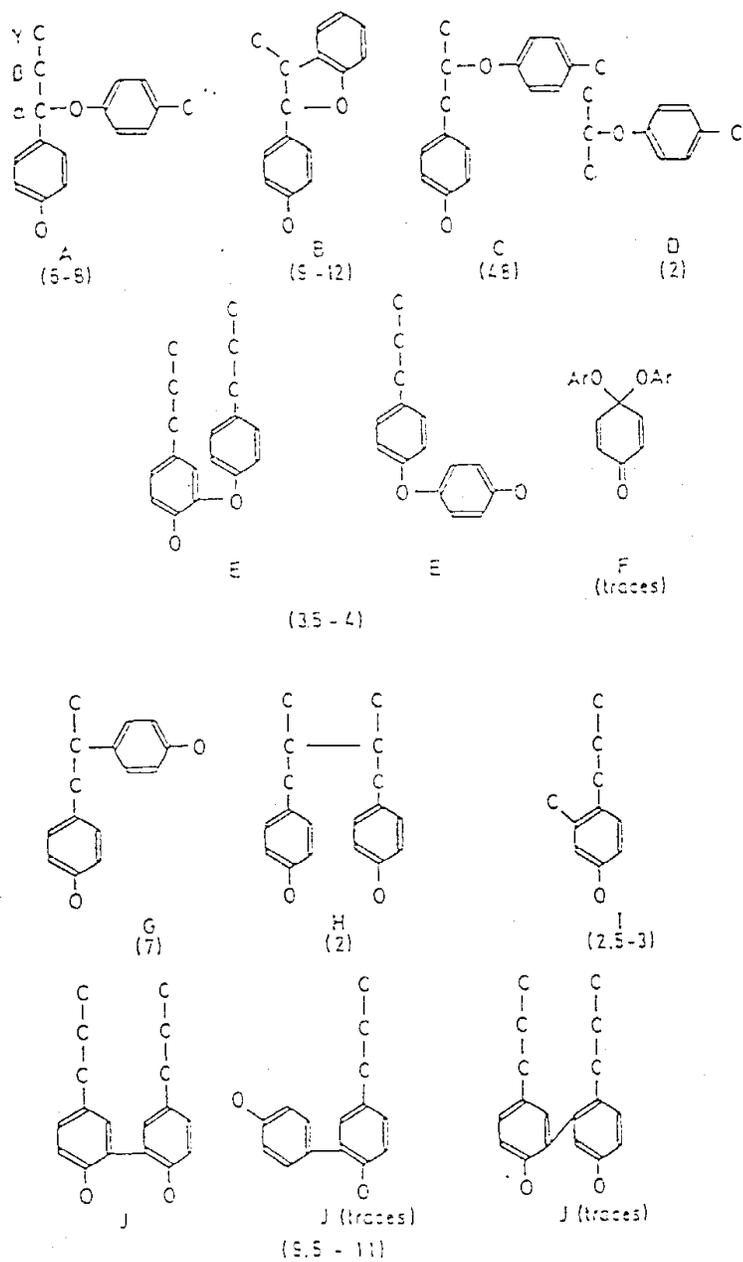


Figure IV – Softwood lignin interconnecting arylpropane unit bonds

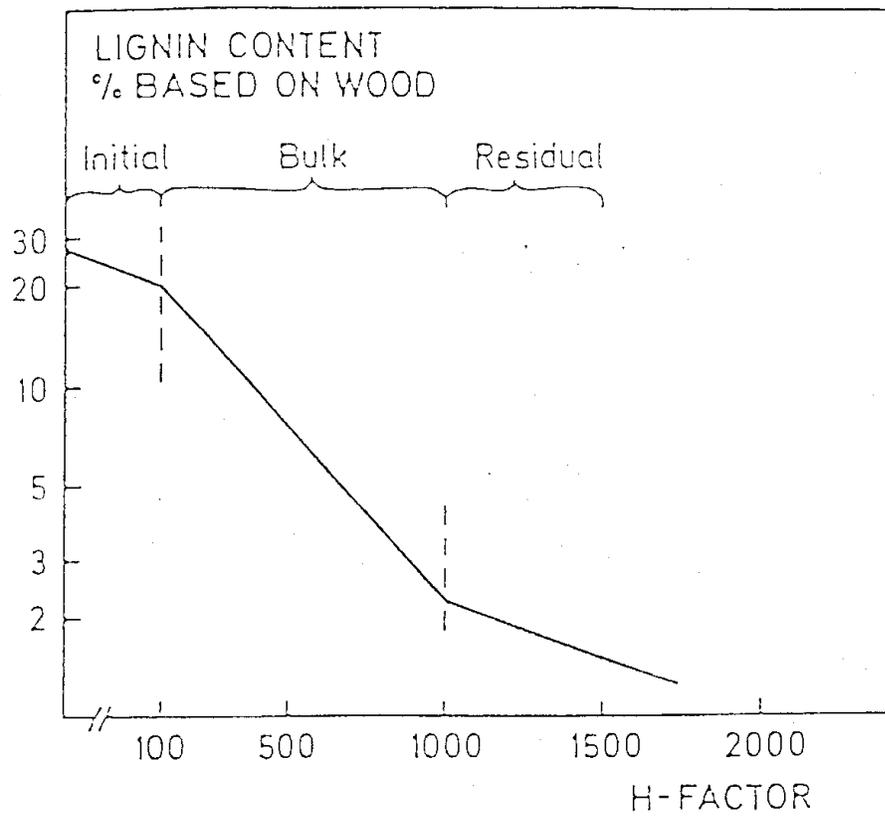


Figure V - Delignification stages in alkaline pulping

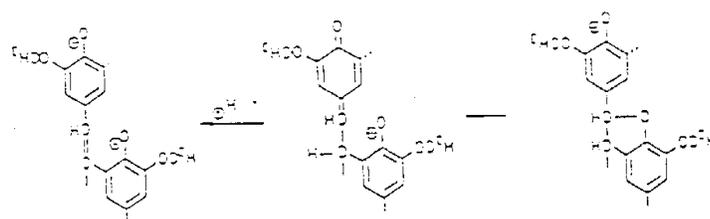


Figure VI – Cleavage of phenolic α aryl ether bonds

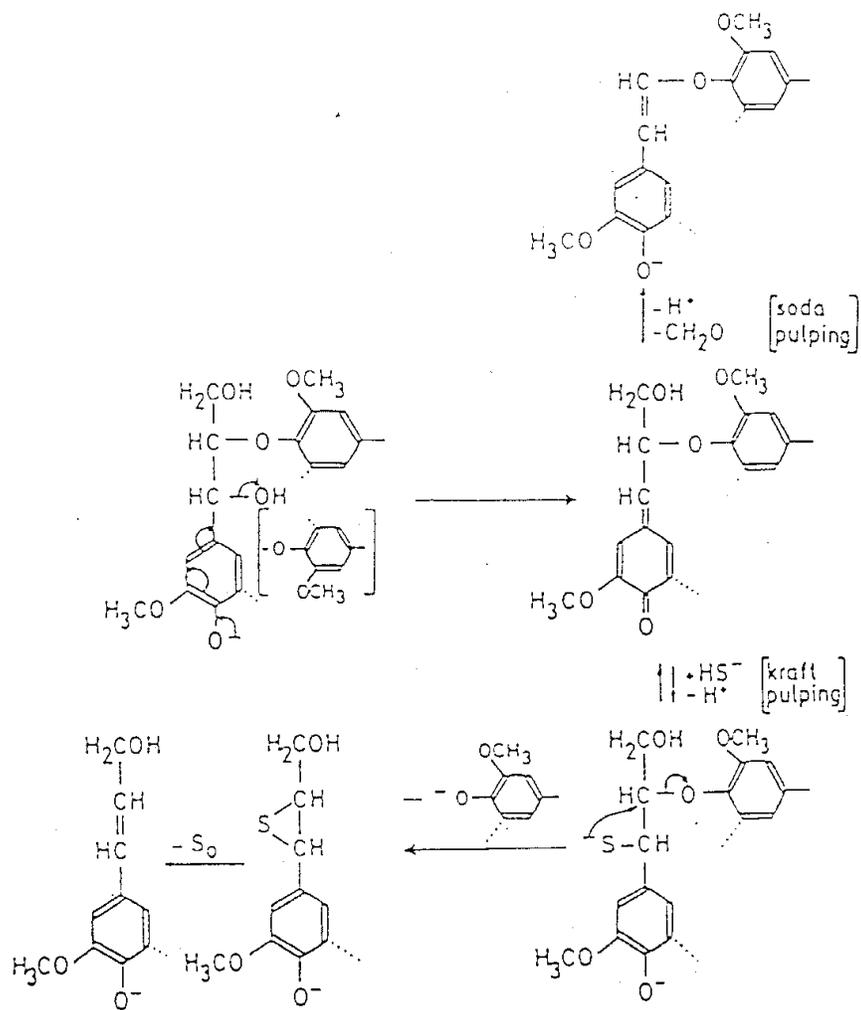


Figure VII – Cleavage of phenolic ether bonds in kraft pulping

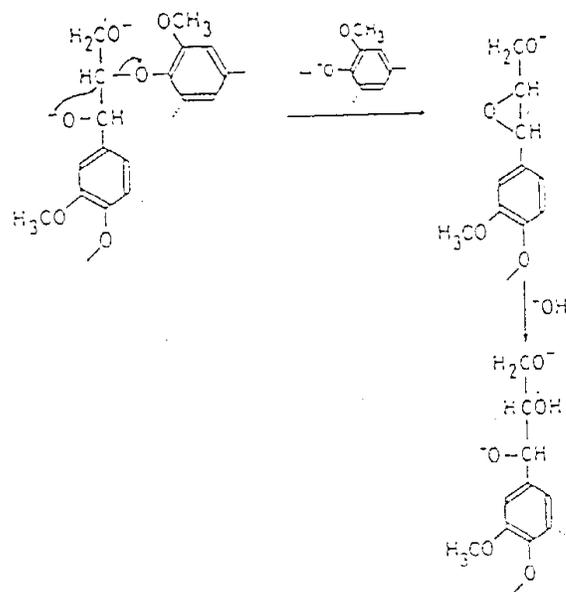
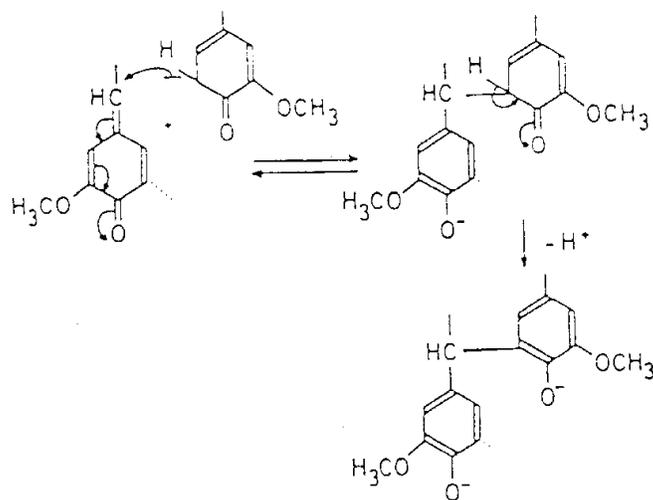
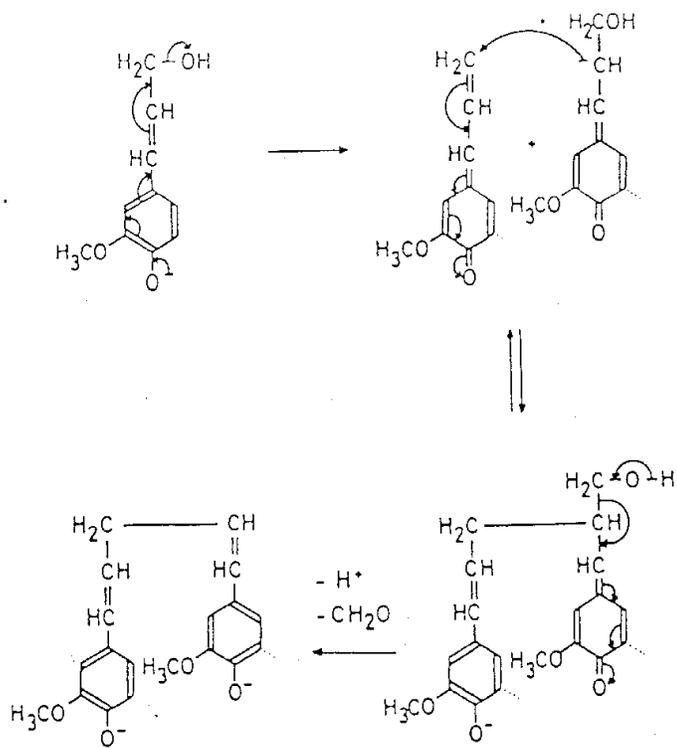


Figure VIII – Cleavage of β aryl ether bonds in non-phenolic structures in alkaline
pulping



Example of primary condensation



Example of secondary condensation

Figure IX – Lignin condensation reactions

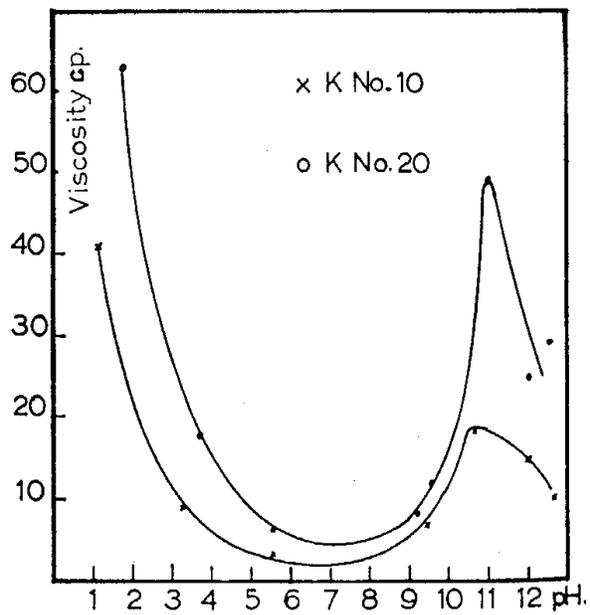


Figure X – Variation of pulp viscosity with pH during sulfite cooking

(Thompson, Peckham and Thode, 40)

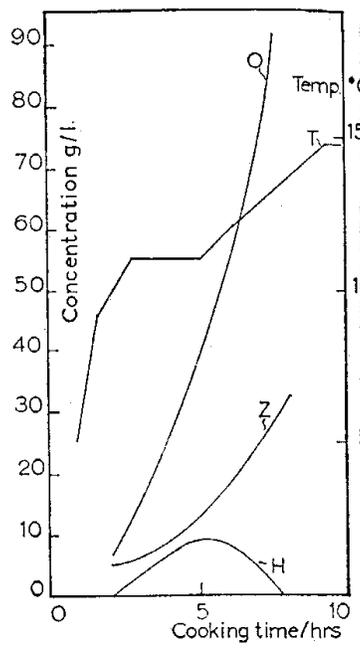


Figure XI – Hemicellulose content in the cooking acid as a function of cooking time
(Erikson and Samuelson, 52)

(T=temperature, O=organic substance g/l, Z=reducing sugars, H=hemicellulose g/l)

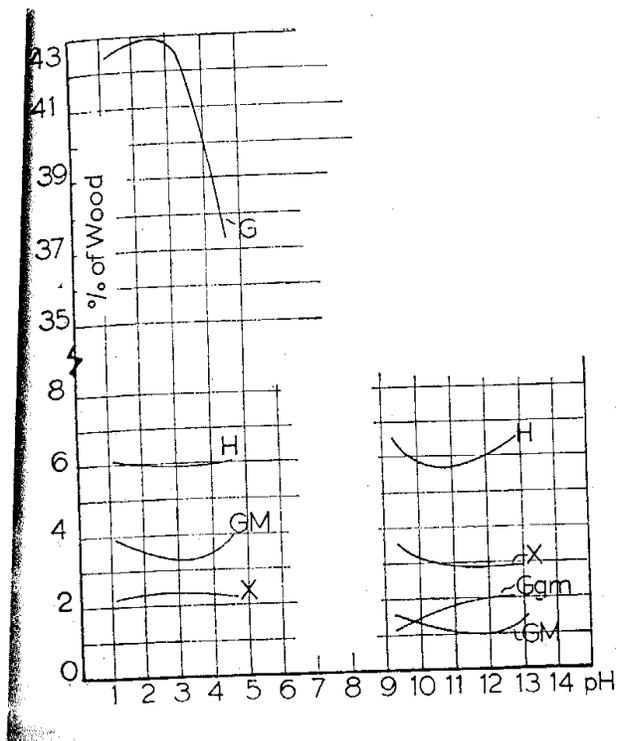


Figure XII – Relation between carbohydrate content of cooking acid and pH in sulfite cooking

(Thompson, Peckham and Thode, 40)

(G=Glucan, H=total hemicellulose, GM=Glucomannan, X=Xylan, Ggm=Galactogluco-mannan, Kappa No=10)

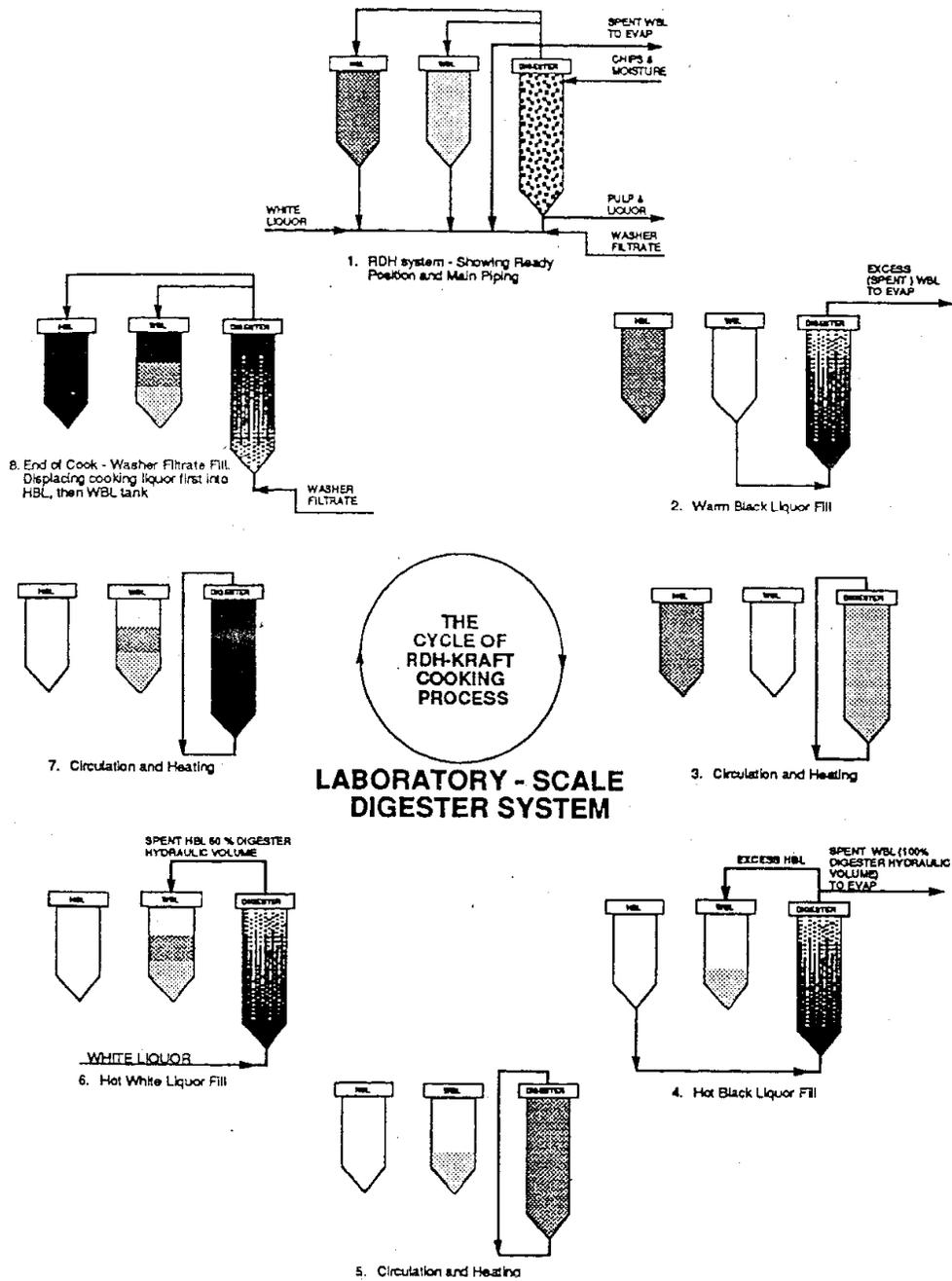


Figure XIII – Cooking cycle of RDH pulping

Sodium Sulfite as a treatment agent in Kraft and RDH pulping

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Abstract

RDH cooks were done using air dried Southern Pine chips with the addition of sodium sulfite in different stages. Sodium sulfite charge was kept at 2% and 4% on OD chips. Improvement in yield and bleachability were not as expected, so to better understand the behaviour of sulfite, it was used as a pre-treatment chemical in modified kraft pulping. Sodium sulfite charge was varied upto 9% on OD chips in modified kraft cooks. Sodium sulfite was added in the pre-cooking stage, cooking and post-cooking stage. The sulfite charge was even split up between pre-treatment and post-treatment. Split addition of sodium sulfite gave good yield. Bleachability, however, didn't show the expected results. Results of this study indicated that RDH cooks with 4% sulfite charge in the C1 (see Experimental Set-up) stage did not show any improvement on yield and bleachability. Split addition (pre-cook and post cook stages) of sulfite charge in the modified kraft cook increased the yield but no improvement in bleachability was seen. 0.1% AQ addition in the modified kraft cook improved the yield, but again no improvement in bleachability was achieved. Further study is needed to better understand the effects of sodium sulfite on the yield and bleachability of pulp. Once the desired results are seen in kraft pulping, RDH should be studied more deeply with sodium sulfite as the treatment chemical.

Introduction

In the last decade, environmental regulations have been focused on the reduction or elimination of chlorine and its derivatives from bleaching operations by alternative bleaching agents and other pulping methods. One of these methods is to use extended

delignification technologies. Extended delignification technology enhances the selectivity in the digester by removal of additional amounts of lignin without decreasing yield.

A disadvantage with the extended delignification process is a yield loss at a kappa of 18-20 for softwoods. This will cause an increase in load going to the recovery. However, use of yield enhancing additives retains more hemicelluloses and increases the pulp yield at a given kappa number. Various additives have been researched, and the most important among them are anthraquinone (AQ), Polysulfide (PS) and Sodium Sulfite (Na_2SO_3).

In this study, we will be looking at sodium sulfite (Na_2SO_3) more closely as an additive in the RDH pulping. Sulfite technology can offer, among other things, higher pulping yield, easier bleaching and higher physical strengths. ⁽¹⁾ Technological advances have rendered sulfite pulping to be an economic and environmentally-attractive alternative to kraft pulping. The main lignin extractor is the sulfite ion and extracts lignin more efficiently than the kraft process. The sulfite ion has been known as the more efficient lignin solubilizer. ⁽²⁾ The sulfonation of lignin is by far the most important reaction when sodium sulfite is present in the cooking liquor ⁽³⁾. The sulfonation of lignin makes it soft and the lignin structure more hydrophilic, thus making the lignin fragmentation easier. The effect of sulfite on wood depends on the pH of the cooking environment. At all pH levels used in sulfite pulping, alpha-carbon position in the lignin molecule is the most active site for reaction with the sulfite ions ⁽⁴⁾. In neutral or alkaline conditions, sulfonation of lignin also takes place in the beta-carbon position. Sulfonation of lignin molecules convert the insoluble and hydrophobic lignin to ligno-sulfonates, which are more soluble and easily fragmented. Sulfonation of lignin takes place over the whole pH range, but decreases as the pH reaches the strongly alkaline range. At this time, activity of the bi-sulfite ion has been overtaken by the activity of hydroxyl ion as the delignification agent ⁽⁵⁾. Thus, by pretreating the wood chips with sodium sulfite, we will get the delignification from sulfonation of lignin, since the pH level will not be highly alkaline at this stage. Further delignification will be achieved in the kraft cooking stage where the pH level is in the strongly alkaline range.

Objective

The purpose of this study is to explore the effects of using sodium sulfite in the different stages of RDH (WBL, C1, C2, HWL – see Experimental Set-up) and kraft pulping (pre-cook, cook and post-cook stage) on yield, residual lignin and bleachability.

Experimental Set-Up

Study of sodium sulfite as a treatment chemical was carried out in the two cooking processes, RDH and Modified Kraft. The RDH process was divided into six stages. All the stages had different chemical charge and temperature.

Weak Black Liquor	WBL1	Stage 1
Weak Black Liquor	WBL2	Stage 2
Hot Black Liquor	C1	Stage 3
Hot Black Liquor	C2	Stage 4
Hot White Liquor	HWL	Stage 5
Wash Filtrate	WF	Stage 6

Liquor profiling was incorporated to distribute the alkali charge throughout the entire cooking process. Sodium sulfite was added in the pre-treatment liquor (black liquor) to study its effect on the yield, delignification rate and bleachability of the pulp. In case of kraft pulping, pre and post treatment was done with sodium sulfite alone. 0.1% AQ was also used in the treatment of chips along with sodium sulfite.

Pulping

RDH

1000gms OD Southern Pine chips were used for cooking. Liquor to wood ratio was maintained at 4:1 for all the cooks. All RDH cooks were charged with 21%AA. H-Factor

was varied from 800 to 2100. Liquor profiling was done in RDH cooks to distribute the alkali charge throughout the whole cooking process. The base case has active alkali divided between different stages as: 3%AA in WBL2, 3% AA in C1, 3% AA in C2 and 12% AA in the cooking liquor. Pre-treatment liquor was heated before being transferred to the digester. This was done to have uniform cooking of the chips and moreover, previous studies have shown that sodium sulfite gives best results in the temperature range of 120°C - 170°C. The temperature of the pre-treatment liquors before being transferred to the digester were :

WBL1	120°C
WBL2	150°C
C1	170°C
C2	170°C
HWL	170°C
WF	120°C

The temperature maintained in the digester during the cooking cycle was :

WBL1	100°C
WBL2	120°C
C1	150°C
C2	165°C
HWL	170°C

Sulfite charge in the pre-treatment stages was based on the OD weight of the pulp. The time-temperature graph is shown in Figure 1. The liquor displacement diagram for RDH is shown in Figure 2.

Modified Kraft

1000gms OD Southern Pine chips were used for all the kraft cooks. 19%AA charge was maintained for the base cook (conventional kraft) at an H-Factor of 1600. Liquor to wood ratio was maintained at 4:1. Sulfite charge varied from 3% to 9%. Chips were treated with sulfite, before, during and after the cook. Treatment liquor was heated to 120°C for one set and to 160°C for another before being transferred to the digester.

Bleaching

Three bleaching sequences were looked upon to study the bleachability of the pulp produced. They were : QP, DEpD₁, DEpD₁ED₂. Except in QP, the final stage was split into 3 parts and the ClO₂ charge was varied from 0.3% to 1.5%.

QP:

<u>Stage</u>	<u>Charge</u>	<u>Final pH</u>	<u>Temperature</u>	<u>Time</u>	<u>Consistency</u>
Q	0.5% DTMPA	5.5-7	70°C	60 min.	5%
P	2%	10.5-11	70°C	120 min.	10%

DEpD₁:

<u>Stage</u>	<u>Charge</u>	<u>Final pH</u>	<u>Temperature</u>	<u>Time</u>	<u>Consistency</u>
D	1.5-3%	2-3	70°C	60 min.	10%
Ep	0.5% H ₂ O ₂ , 0.5% NaOH for every 1% ClO ₂ .	10.3-10.8	70°C	60 min.	10%
D ₁	0.5-1.5%	–	70°C	180 min.	10%

DEpD₁ED₂:

<u>Stage</u>	<u>Charge</u>	<u>Final pH</u>	<u>Temperature</u>	<u>Time</u>	<u>Consistency</u>
D	1.5-3%	2-3	70°C	60 min.	5%
Ep	0.5% H ₂ O ₂ , 0.5% NaOH for every 1% ClO ₂ .	10.3-10.8	70°C	60 min.	10%
D ₁	1%	3.5-4.0	70°C	60 min.	10%
E	0.8%	10.5-11	70°C	60 min.	10%
D ₂	0.3-0.7%	–	70°C	180 min.	10%

Results & Discussion

RDH cooks were done with 2% sodium sulfite charge in the pre-treatment stages. 2% sulfite charge in the WBL2 and C2 stages showed improvement in yield compared to the base cook but the delignification rate went down. 2% sulfite charge in the C1 stage showed improvement in yield compared to the base cook and delignification rate was comparable to the base cook. As shown in Figures 3 and 4, performance of sulfite on yield and delignification rate was best when sulfite was added in the C1 stage. Pre-treatment liquor in the C1 stage was heated to a temperature of 150°C, which is in the range specified for best performance of sodium sulfite (120°C – 165°C). No appreciable change was noticed in the bleachability of the pulp (Figure 5). Sulfite charge was increased to 4% in C1 stage. As shown in Figures 6 and 7, results didn't show appreciable improvement compared to base cook or 2% cook. Low sulfite charge could have been the possible reason in the current experimental setup for low delignification rate and lower bleachability. Higher charges of sulfite may bring about better delignification, thus resulting in higher bleachability. To better understand the behaviour of sodium sulfite as a treatment agent, sulfite treatment was studied in kraft pulping. The experimental data from the RDH cooks is included in Table 1.

Kraft cooks were started with H-Factor of 1600 and 19% AA charge. Pre-treatment liquor (sodium sulfite + water) was heated to 120°C before being transferred to the digester. Sulfite charge was varied from 3-9%. The results are shown in Figures 8, 9 and 10. Brightness went down compared to the base case (conventional kraft). So, the temperature of the pre-treatment liquor was raised to 160°C, as sulfite is most effective in the temperature range of 120-165°C. Results thus obtained are shown in Figures 11, 12 and 13. Yield, delignification rate and bleachability showed improvement. Post-treatment (treatment of chips with sulfite liquor after the cook) was also looked into with sulfite charge being varied from 3-9%. Results were the same as obtained with sulfite as a pre-treatment agent. (Figures 14, 15, 16) As the sulfite charge was increased, bleachability improved. Thus, suggesting the trend that increased sulfite charge could result in even better results i.e. selective delignification and increase in brightness of the pulp.

9% sulfite charge was used for further study. It was split up equally between pre and post treatment stages. (Figure 17, 18 and 19) There was no appreciable change in the bleachability. The reason could be the difference in kappa number between the test cooks (chips treated with sulfite) and the base cook. To better study the bleachability, kappa numbers need to be comparable in the test cooks and the base cook. To achieve this, active alkali charge was reduced to 15%AA for test cooks, H-Factor being kept constant at 1600. 0.1% AQ was added with sulfite in the pre and post treatment stages. The difference in the yield could be easily noticed (Figures 20 and 21). The bleachability results obtained were still not very encouraging (Figure 22) indicating ineffectiveness of sulfite charge at temperatures lower than the cooking temperature. The possible reason could be the high kappa number i.e. more lignin as a result of less delignification and low active alkali charge.

Conclusion

1. In RDH cooks, sulfite pre-treatment in C1 stage was the most effective with good yield and delignification. No improvement in bleachability.
2. In Kraft cooks, pre, post and split treatment with sulfite at 160°C resulted in better delignification rate but the yield dropped compared to the base case i.e. conventional kraft cook. Bleachability showed minimal improvement.
3. When active alkali of sulfite split treated kraft cook was dropped to 15%, yield improved a lot but the brightness went down.
4. 0.1% AQ addition in the pre-treatment stage along with sulfite split treatment in 15% AA kraft cook resulted in better yield but no change in bleachability.
5. Sulfite treatments in RDH and Kraft cooks did improve yield and delignification, but didn't show improvement in bleachability. Sulfite is known to improve bleachability when used as a cooking chemical, but it didn't show the expected results when used as a pre-treatment/post-treatment agent.

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<u>H-Factor</u>	<u>Kappa Number</u>	<u>Yield</u>	<u>Brightness</u>	<u>Brightness</u>	<u>Kappa Number</u>	<u>Yield</u>	<u>Brightness</u>	<u>Brightness</u>	<u>Kappa Number</u>
	<i>base</i>	<i>base</i>	<i>base unbleached</i>	<i>base bleached</i>	<i>2% WBL</i>	<i>2% WBL</i>	<i>2% WBL unbleached</i>	<i>2% WBL bleached</i>	<i>2% C1</i>
600	45.68	43.7	22.38	31.09	43.13	45.82	21.82	30.94	40.57
700	31.57	41.5							32.8
800	24.94	40.5							21.68
1000					31.74	41.37	24.81	38.64	
1100	25.37	40.77	28.46	41.56					
1200	22.53	39.11	29.39	43.45					
1400					25.77	40.5	27.14	41.16	18.97
1600	15.13	39.24	34.11	48.28					
1800					16.32	38.67	31	48.01	17.68

<u>H-Factor</u>	<u>Yield</u>	<u>Brightness</u>	<u>Brightness</u>	<u>Kappa Number</u>	<u>Yield</u>	<u>Brightness</u>	<u>Brightness</u>	<u>Kappa Number</u>	<u>Yield</u>
	<i>2% C1</i>	<i>2% C1 unbleached</i>	<i>2% C1 bleached</i>	<i>2% C2</i>	<i>2% C2</i>	<i>2% C2 unbleached</i>	<i>2% C2 bleached</i>	<i>4% C1</i>	<i>4% C1</i>
600	44.36	23	33.02	51.18	44.04	18.79	23.91		
700									
800	43.48							41.91	45.54
1000	41.91	29.93	45.52	34.18	43.19	24.81	34.62		
1100									
1200								29.96	43.35
1400	39.79	29.5	46.32	27.04	42.21	27.29	36.21		
1600								20.56	41.21
1800	38.71	28.75	46.34						

Table 1 – RDH experimental data

Time vs. Temp.

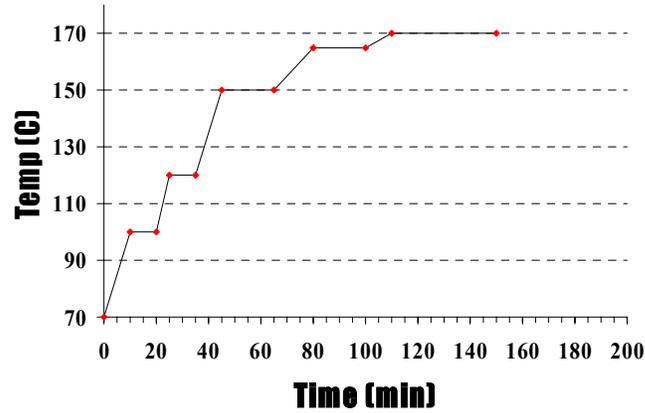


Figure 1 – Time-Temperature curve of the RDH process

Displacement Sequence

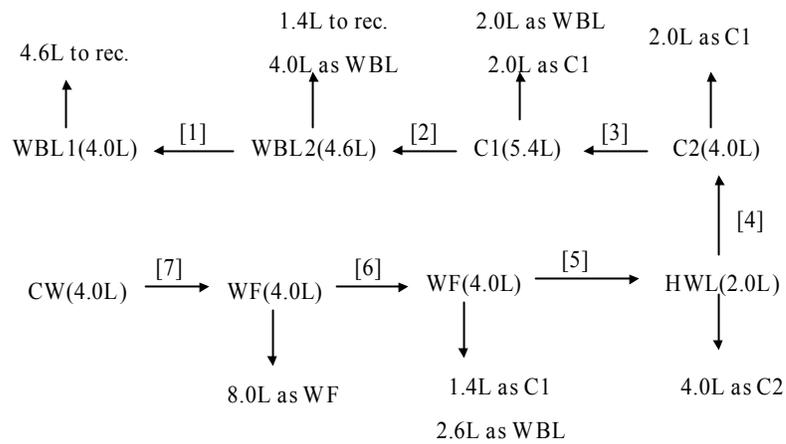


Figure 2 – Flowchart of the RDH process

Yield Vs Kappa

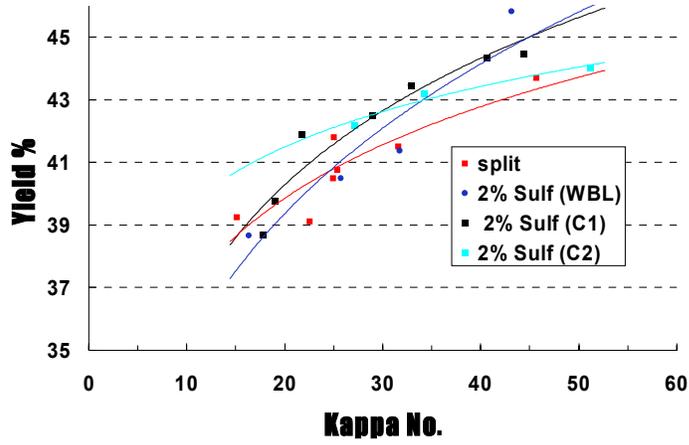


Figure 3 -2% sulfite in WBL, C1 and C2 compared to the base case

H-Factor Vs Kappa No.

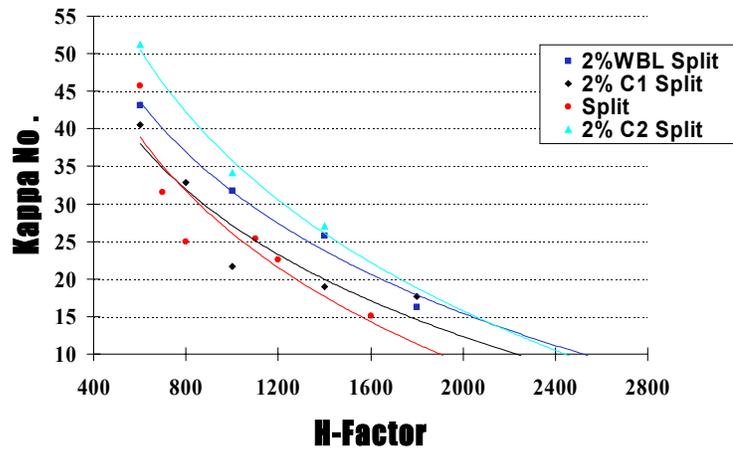


Figure 4 - 2% sulfite in WBL, C1 and C2 compared to the base case (delgnification rate)

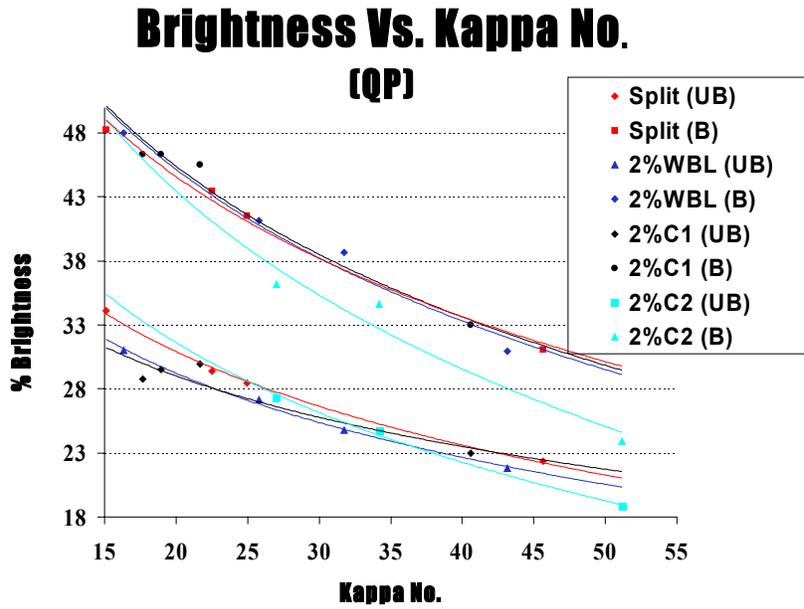


Figure 5 – Brightness measured after QP bleaching process, as a function of kappa number

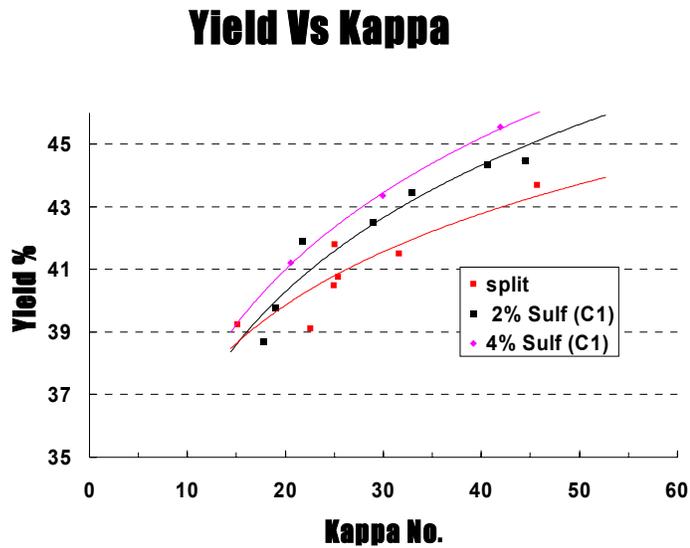


Figure 6 – 2% sulfite and 4% sulfite in C1 compared to the base case

H-Factor Vs Kappa No.

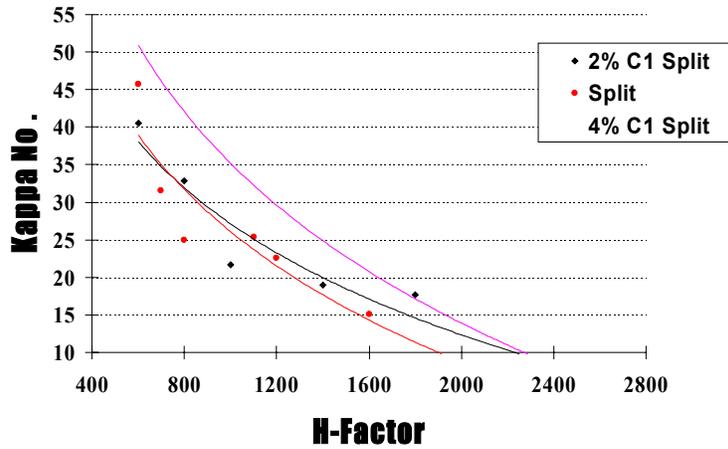


Figure 7 - 2% sulfite and 4% sulfite in C1 compared to the base case (delignification rate)

Yield Vs Kappa (pre-treatment at 120°C)

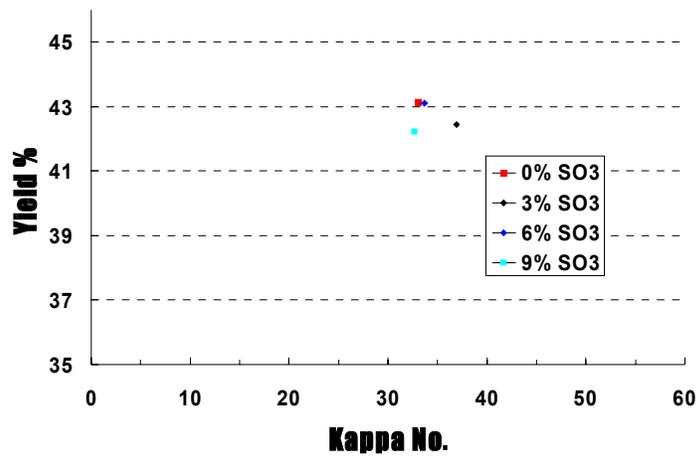


Figure 8 – Pre-treatment with sulfite in conventional kraft at 120°C

H-Factor Vs Kappa No. (pre-treatment at 120C)

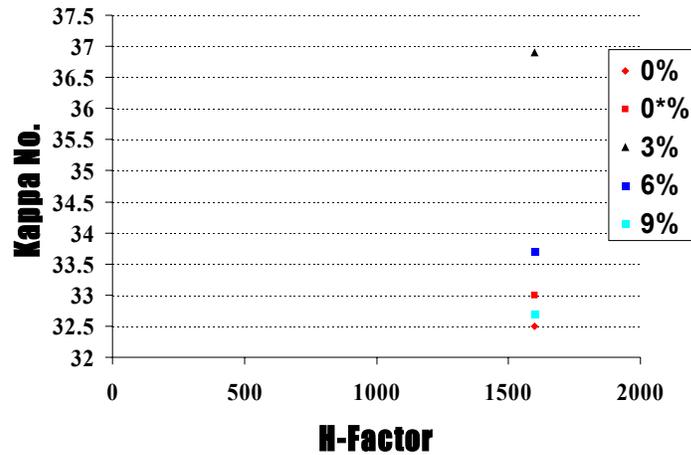


Figure 9 - Pre-treatment with sulfite in conventional kraft at 120°C (delignification rate)

Brightness as a function of Chlorine Dioxide Charge {D₀(EP)D₁}

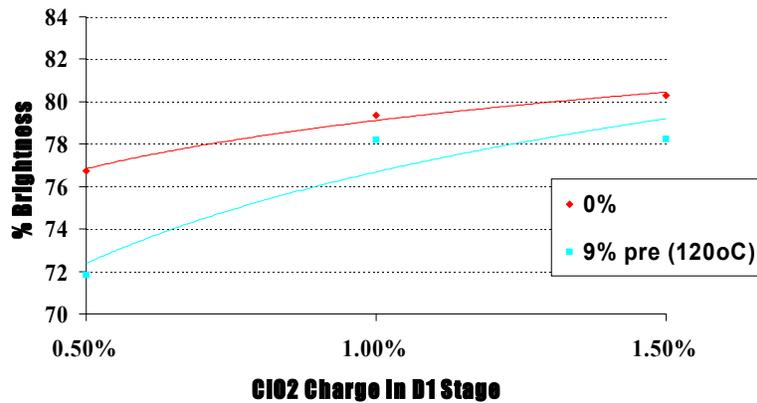


Figure 10 – Brightness as a function of chlorine charge in D1 stage (pre-treatment 120°C)

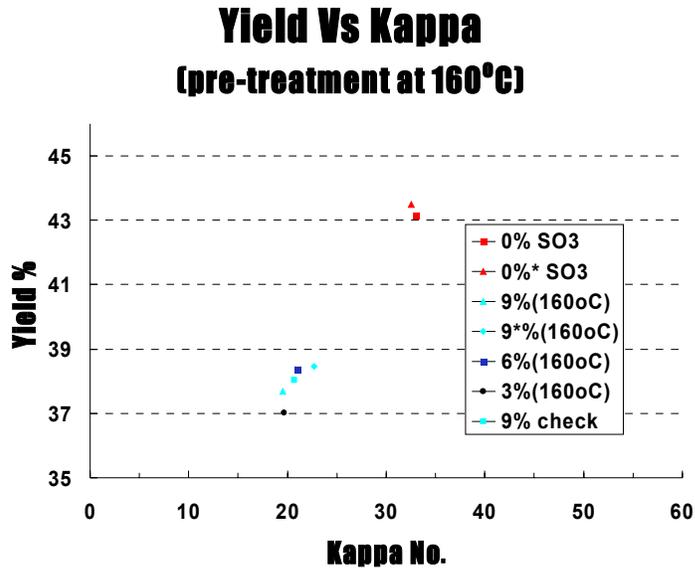


Figure 11 - Pre-treatment with sulfite in conventional kraft at 160°C

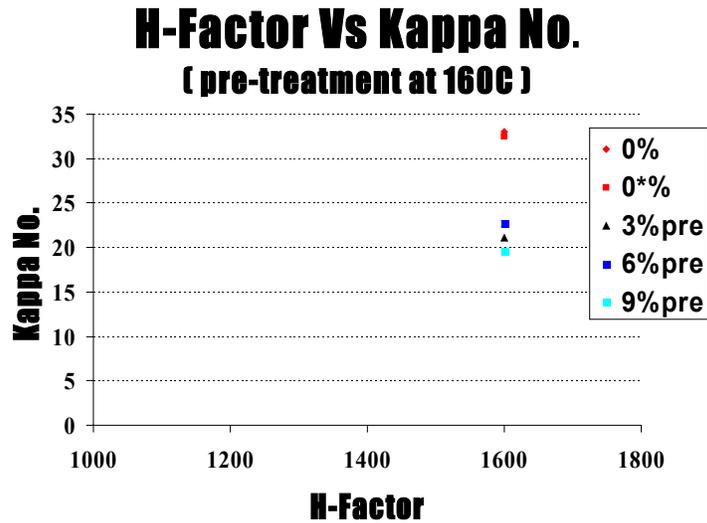


Figure 12 - Pre-treatment with sulfite in conventional kraft at 160°C (delignification rate)

Brightness as a function of Chlorine Dioxide Charge {D₀(EP)D₁}



Figure 13 - Brightness as a function of chlorine charge in D1 stage (pre-treatment 160°C)

Yield Vs Kappa (post-treatment at 160°C)

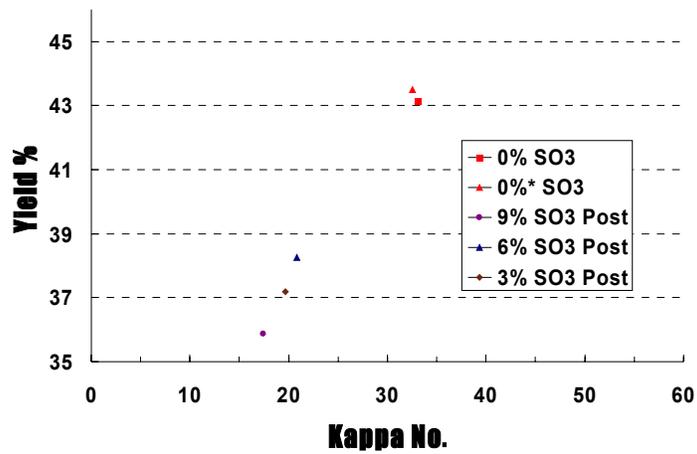
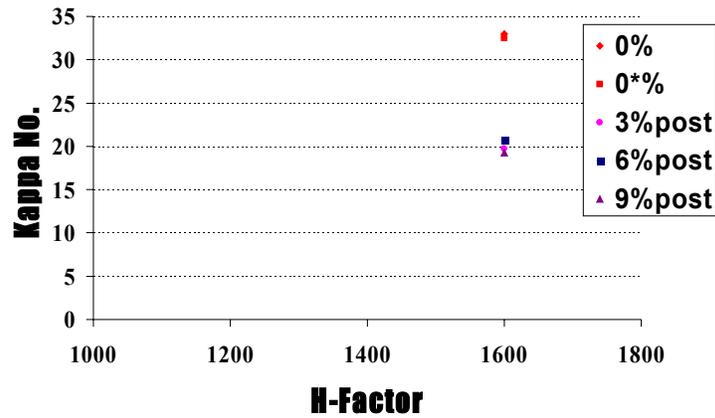


Figure 14 - Post-treatment with sulfite in conventional kraft at 160°C

H-Factor Vs Kappa No. (post-treatment at 160C)



**Figure 15 - Post-treatment with sulfite in conventional kraft at 160°C
(delignification rate)**

Brightness as a function of Chlorine Dioxide Charge {D₀(EP)D₁}



**Figure 16 - Brightness as a function of chlorine charge in D1 stage (post-treatment
160°C)**

Yield Vs Kappa (treatment at 160°C)

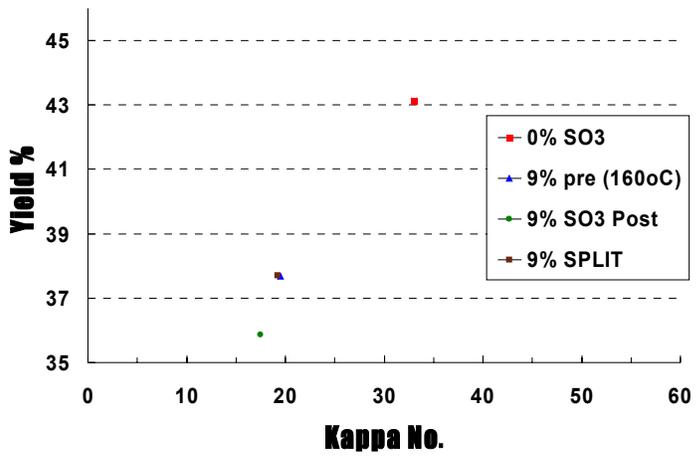


Figure 17 – Summary of sulfite treatment in conventional kraft at 160°C

Brightness as a function of Chlorine Dioxide Charge {D₀(EP)D₁}

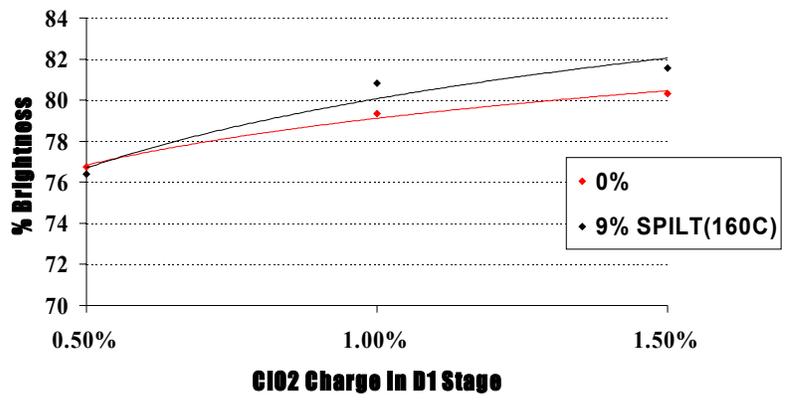


Figure 18 – Brightness as a function of chlorine charge in D1 stage(sulfite charge split in pre-cook and post-cook stage at 160°C)

Brightness as a function of Chlorine Dioxide Charge {D₀(EP)D₁}

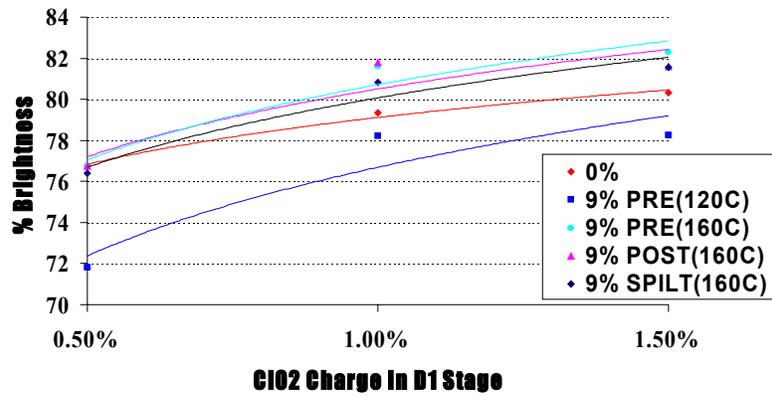


Figure 19 – Summary of sulfite charge and it's affect on brightness

Yield Vs Kappa (treatment at 160°C)

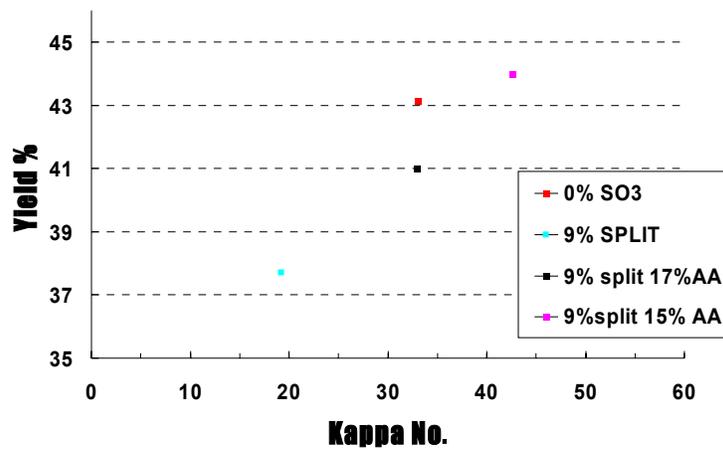


Figure 20 – Summary of sulfite treatment (varying active alkali)

Yield Vs Kappa (treatment at 160°C)

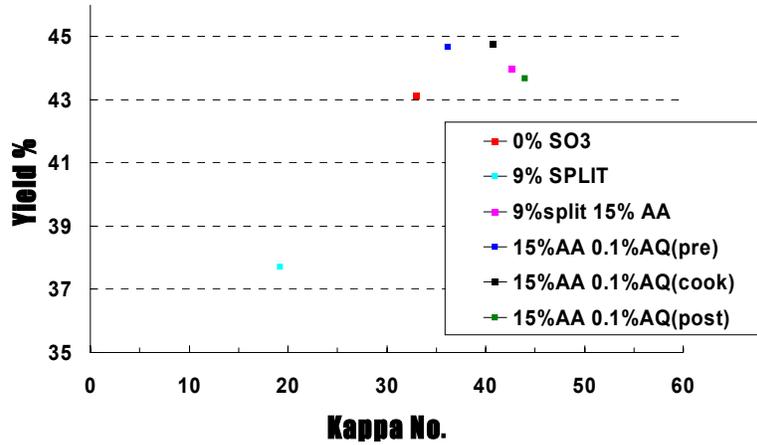


Figure 21 – Summary of sulfite treatment with 0.1% AQ

Brightness as a function of Chlorine Dioxide Charge {D₀(EP)D₁ED₂}

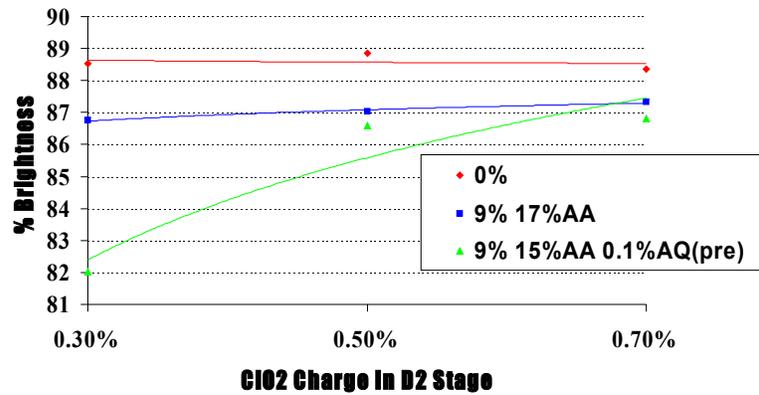


Figure 22 – Summary of affect of sulfite treatment with 0.1% AQ in brightness

Study of treatment with different sulfidity liquors in Kraft pulping

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Abstract

Sulfide concentration is a crucial factor in kraft pulping. This study looks into the effects of sulfidity on the yield and kappa number in kraft pulping. Sulfidity was varied from 0-100% in all the stages in a 3-stage modified kraft pulping process. Pre-treatment of chips with sodium sulfide resulted in lower kappa number. Yield was higher for cooks at lower H-Factor. Higher sulfidity in the cooking stage gave higher yield at high H-Factor. The results obtained from the experimental and model data indicated that sodium sulfide treatment in the pre-treatment (pre-cook) stage is the most affective with regards to yield and kappa number. The sulfide concentration in the post-treatment (post-cook) stage had no substantial effect on kappa number and yield. These results can be used to optimize the pretreatment/cooking conditions in a modified batch cooking process.

Introduction

The kraft process is the dominating process for the production of chemical pulp in the world for the following reasons:

1. Simplicity.
2. Insensitivity to variations in wood properties.
3. Applicable to wide spectrum of wood species.
4. Good properties of pulp produced.

It does have some disadvantages too. The one which is of most importance is amount of residual lignin remaining after the cook. This residual lignin is very difficult to remove,

with the risk of polysaccharides degradation. The residual lignin can be greatly reduced by modifying the kraft process and introduce the concept of extended delignification. One of the advantages of extended delignification is the lower consumption of bleaching chemicals, due to lower amounts of residual lignin.

The four basic principles proposed by Teder ⁽¹⁾, which need to be followed for extended delignification are:

1. Level out the alkali concentration – High level of alkali at the beginning of the cook leads to carbohydrate degradation due to primary and secondary peeling reactions. The organic acids formed during this process consume about 70% of the alkali, thus leaving very little for lignin degradation. Other side-effect is that the acids produced lead to lignin condensation, thus increased amount of residual lignin.
2. Keep the HS⁻ concentration high, especially at the start of the cook – High sulfidity at the start of the cook will provide a faster delignification rate and to some extent prevent condensation reactions.
3. Keep the dissolved lignin and Na⁺ concentration low towards the end of the cook – Ionic strength in the cook has been found to be directly proportional to the amount of residual lignin. Some studies have shown that the presence of lignin in the cooking liquor during the final phase of pulping hurts the selectivity and reduces the delignification rate.
4. Keep the temperature low, especially at the start and end of the cook – The primary advantage by lower temperature will be low fiber damage during the blow out after pulping. Degradation of carbohydrates is also substantially reduced at low temperatures.

Sodium sulfide plays an important role in the delignification of wood, when added at different stages of kraft pulping. It has been established that the kappa number is inversely proportional to the sulfidity in the cooking liquor.⁽²⁾ Delignification in kraft pulping process can be divided into three stages: “initial”, “bulk” and “residual”. The deficiency of sulfide seems to appear in the beginning of the conventional kraft cook ⁽³⁾. During the initial part of the cook, sulfide exists in the liquor in a weakly bound form,

besides being chemically bound to the lignin and as free HS⁻ ions. The amount of this weakly bound HS⁻ can be so large that free HS⁻ ion concentration, essential for selective delignification, is seriously decreased. ⁽⁴⁾ It is known that shortage of hydrogen sulfide ions during the transition from initial to bulk phase (at 150°C) leads to the formation of stable enol ether structures in the residual lignin⁽¹⁾, since they are formed from beta-aryl ether linkages in alkaline conditions. These structures are detrimental to the bleachability and hinder the ability to cook low kappa pulps. Moreover, Hydrosulfide content in the initial part of the bulk delignification shows the highest impact on delignification efficiency. ⁽⁵⁾

As stated earlier as one of the principles of extended delignification, high sulfide concentration during the early stages of the cook increases the rate of delignification and also minimizes the condensation reactions. Earlier studies have shown that the chips absorb sulfide from liquors contains sulfur ⁽⁴⁾, thus increasing the rate of delignification in the bulk phase.

Objective

The purpose of this study is to take advantage of the principles of extended delignification and apply it to the modified kraft pulping process using sodium sulfide for higher yield and lower kappa number (lower residual lignin). The experimental results will help design a model for optimum yield and kappa number. The counter-current displacement of liquors in the cooking process will make use of the known benefit that hydrosulfide in the recirculated black liquors play a controlling role in the terms of delignification rate and selectivity. ⁽⁵⁾

Experimental Setup

This study was done on a 3-stage modified kraft pulping process. The 3 stages are:

Pre-treatment	Stage 1 (A)
Cooking	Stage 2 (B)
Post-treatment	Stage 3 (C)

Liquor in all the three stages was comprised of NaOH and Na₂S, the percentage of each being varied in each stage in each cook. Sulfidity of liquors was varied from 0-100 %, maintaining 21%AA. Cooking temperature is maintained at 170°C. H-Factor is varied from 1500 to 2100. The pre-treatment liquor is heated to 160°C before being transferred to the digester. The chips are then treated for 1hr. The pre-treatment liquor is counter-currently displaced with cooking liquor. Post-treatment liquor counter-currently displaces the cooking liquor when H-Factor is reached and the chips are then post-treated for 1hr. Three sets of nine cooks each were carried out with different composition of liquors. The sulfide charge distribution was done as follows:

<u>Pre</u>	<u>Cook</u>	<u>Post</u>
0	0	0
0	0	100
0	100	0
0	100	100
100	0	0
100	0	100
100	100	0
100	100	100
50	50	50

The above table shows the percent sulfidity of the liquor in each stage.

Results & Discussion

The experimental study was divided into three sets of 9 cooks each, based on the final H-Factor. The results are in Tables A, B and C. A model was developed for kappa number

and yield using the SAS system which used the REG procedure, the experimental data being the input. The results generated by the SAS system are shown in Table D and Table E. Table D contains the statistical data for kappa number and Table E contains the statistical data for yield.

The model developed for yield was dependent on the following variables:

1. A^2
2. $A*H$
3. $B*H$

Model Equation:

$$\text{Yield} = 47.59710 + 0.00074276*A^2 - 0.00004944*A*H - 0.00001212*B*H$$

The model developed for kappa number was dependent on the following variables:

1. A
2. H^2
3. A^2
4. B

Model Equation:

$$\text{Kappa} = 92.35155 - 0.84202*A - 0.15373*B + 0.00717*A^2 - 0.00000707*H^2$$

Where symbols shown in the above equations are:

A – Sulfidity in pre-treatment stage

B – Sulfidity in cooking stage

H – H-Factor

* - Symbol for multiplication

The experimental results were compared with the model results. The kappa number and yield calculated using the models are shown in Tables F, G and H. Figure A (kappa number) and Figure B (yield) show the same trend for experimental results and model results. This validates the equations derived from the models. Thus, a conclusion can be drawn that the variables (yield and kappa number) are dependent on the parameters chosen by the model, as shown by the equations above.

The model was further used to study the effect of various parameters on kappa number and yield.

Figure C and Figure D have H-factor constant at 2100. Sulfidity in each stage was varied from 0-100%, keeping the sulfidity in others stages constant at 0%. Eg. Stage A – 100%, Stage B – 0%, Stage C – 0%. Increase in sulfidity was most effective in the pre-treatment stage (A) as it gave lowest kappa number for 50-70% sulfidity range. Yield also showed maximum increase for increase in sulfidity for 50-100% sulfidity range.

Figure E and Figure F have H-factor varied from 1200 to 2000. These graphs show that increase of sulfidity in pre-treatment stage (A) results in highest drop in kappa number. Loss of yield, though, was more in this stage for high H-Factor cooks.

Figure G is a plot of Yield Vs Kappa Number for values obtained from the model. The sulfidity in each stage is varied from 0-100%, keeping the sulfidity in other stages constant at 0%. H-Factor is maintained at 2100. As shown in the graph, yield is higher and kappa is lower when sulfidity is increased in the pre-treatment stage (A).

Figure H is a plot of Yield Vs Kappa Number for Model and Experimental values. The trends shown by Model and Experimental values are the same, thus reaffirming the validity of the model developed.

Conclusion

Above discussion shows that increase of sulfidity in pre-treatment stage (A) gives the best results for kappa number and yield. Yield loss is less for high H-Factor cooks when sulfidity is increased in the cooking stage. Study of both sets (Set 1 – Figures C and D, Set 2 – Figures E and F) in our experimental setup showed that higher sulfide charge in pre-treatment stage (A) is required for higher yield and lower kappa number. Depending on the end result desired, sulfidity in cooking stage (B) can be varied. The model showed

that post-treatment stage (C) had insignificant effect on the kappa number and yield of the pulp.

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Table A

Experimental results for H-Factor = 1500

<u>Cook no.</u>	<u>% Sulfidity</u>			<u>HF = 1500</u>			
	A	B	C	<u>Kappa No.</u>	<u>% Yield</u>	<u>% Rejects</u>	<u>%Total Yield</u>
1	0	0	0	81.72	31.67	21.65	53.32
2	0	0	100	78.06	42.72	6.19	48.91
3	0	100	0	58.53	42.43	1.13	43.56
4	0	100	100	59.18	43.46	4.12	47.58
5	100	0	0	62.93	43.51	3.40	46.91
6	100	0	100	61.49	44.44	2.37	46.81
7	100	100	0	53.94	44.01	4.93	48.94
8	100	100	100	51.56	43.12	3.09	46.21
9	50	50	50	45.69	43.22	1.03	44.25

Table B

Experimental results for H-Factor = 1800

<u>Cook no.</u>	<u>% Sulfidity</u>			<u>HF = 1800</u>			
	A	B	C	<u>Kappa No.</u>	<u>% Yield</u>	<u>% Rejects</u>	<u>%Total Yield</u>
1	0	0	0	70.92	40.15	8.97	49.12
2	0	0	100	65.79	41.52	2.06	43.58
3	0	100	0	54.48	42.51	1.03	43.54
4	0	100	100	45.75	44.24	1.65	45.89
5	100	0	0	58.39	42.79	1.75	44.54
6	100	0	100	49.06	42.86	1.24	44.10
7	100	100	0	42.33	43.5	1.13	44.63
8	100	100	100	40.22	41.25	1.03	42.28
9	50	50	50	38.29	43.85	0.72	44.57

Table C

Experimental results for H-Factor = 2100

<u>cook no.</u>	<u>% Sulfidity</u>			<u>HF = 2100</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>Kappa No.</u>	<u>% Yield</u>	<u>% Rejects</u>	<u>%Total Yield</u>
1	0	0	0	69.28	38.42	10.05	48.47
2	0	0	100	63.88	44.13	1.55	45.68
3	0	100	0	45.61	42.58	1.03	43.61
4	0	100	100	42.63	43.14	1.97	45.11
5	100	0	0	49.65	43.65	1.03	44.68
6	100	0	100	41.65	44.03	1.86	45.89
7	100	100	0	35.62	42.31	0.92	43.23
8	100	100	100	38.49	41.26	1.03	42.29
9	50	50	50	27.42	42.11	0.41	42.52

Table D

Model for Kappa Number – R = 0.9128, F Value = 57.59

<u>Variable</u>	<u>Parameter Estimate</u>	<u>Standard Error</u>	<u>Type II SS</u>	<u>F Value</u>	<u>Pr > F</u>
<u>Intercept</u>	92.35155	3.45142	13275	715.97	< 0.0001
<u>A</u>	-0.84202	0.10693	1149.71687	62.01	< 0.0001
<u>B</u>	-0.15373	0.01758	1418.03627	76.48	< 0.0001
<u>A2</u>	0.00717	0.00105	855.85927	46.16	< 0.0001
<u>H2</u>	-0.00000707	9.386451E-7	1053.19947	56.80	< 0.0001

A – Sulfidity in pre-treatment stage

B – Sulfidity in cooking stage

H – H-Factor

Table E

Model for Yield – R = 0.4393, F Value = 6.01

<u>Variable</u>	<u>Parameter Estimate</u>	<u>Standard Error</u>	<u>Type II SS</u>	<u>F Value</u>	<u>Pr > F</u>
Intercept	47.59710	0.69588	19591	4678.37	< 0.0001
A2	0.00074276	0.00032704	21.59947	5.16	0.0328
AH	-0.00004944	0.00001807	31.34344	7.48	0.0118
BH	-0.00001212	0.00000457	29.51669	7.05	0.0142

A – Sulfidity in pre-treatment stage

B – Sulfidity in cooking stage

H – H-Factor

Table F

Model results for H-Factor = 1500

	<u>% Sulfidity</u>			<u>HF = 1500</u>	
<u>cook no.</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>Kappa No.</u>	<u>%Total Yield</u>
1	0	0	0	76.44	47.60
2	0	0	100	76.44	47.60
3	0	100	0	61.07	45.78
4	0	100	100	61.07	45.78
5	100	0	0	63.94	47.61
6	100	0	100	63.94	47.61
7	100	100	0	48.57	45.79
8	100	100	100	48.57	45.79
9	50	50	50	44.58	44.84

Table G

Model results for H-Factor = 1800

<u>cook no.</u>	<u>% Sulfidity</u>			<u>HF = 1800</u>	
	A	B	C	<u>Kappa No.</u>	<u>%Total Yield</u>
1	0	0	0	69.44	47.60
2	0	0	100	69.44	47.60
3	0	100	0	54.07	45.42
4	0	100	100	54.07	45.42
5	100	0	0	56.94	46.13
6	100	0	100	56.94	46.13
7	100	100	0	41.57	43.94
8	100	100	100	41.57	43.94
9	50	50	50	37.58	43.91

Table H

Model results for H-Factor = 2100

<u>cook no.</u>	<u>% Sulfidity</u>			<u>HF = 2100</u>	
	A	B	C	<u>Kappa No.</u>	<u>%Total Yield</u>
1	0	0	0	61.17	47.60
2	0	0	100	61.17	47.60
3	0	100	0	45.80	45.05
4	0	100	100	45.80	45.05
5	100	0	0	48.67	44.64
6	100	0	100	48.67	44.64
7	100	100	0	33.30	42.10
8	100	100	100	33.30	42.10
9	50	50	50	29.31	42.99

Table I

Model And Experimental Results at a Glance

<u>H-Factor</u>	<u>Model Yield</u>	<u>Experimental Yield</u>	<u>Model Kappa Number</u>	<u>Experimental Kappa Number</u>
1500	47.60	53.32	76.44	81.72
1500	47.60	48.91	76.44	78.06
1500	45.78	43.56	61.07	58.53
1500	45.78	47.58	61.07	59.18
1500	47.61	46.91	63.94	62.93
1500	47.61	46.81	63.94	61.49
1500	45.79	48.94	48.57	53.94
1500	45.79	46.21	48.57	51.56
1500	44.84	44.25	44.58	45.69
1800	47.60	49.12	69.44	70.92
1800	47.60	43.58	69.44	65.79
1800	45.42	43.54	54.07	54.48
1800	45.42	45.89	54.07	45.75
1800	46.13	44.54	56.94	58.39
1800	46.13	44.1	56.94	49.06
1800	43.94	44.63	41.57	42.33
1800	43.94	42.28	41.57	40.22
1800	43.91	44.57	37.58	38.29
2100	47.60	48.47	61.17	69.28
2100	47.60	45.68	61.17	63.88
2100	45.05	43.61	45.80	45.61
2100	45.05	45.11	45.80	42.63
2100	44.64	44.68	48.67	49.65
2100	44.64	45.89	48.67	41.65
2100	42.10	43.23	33.30	35.62
2100	42.10	42.29	33.30	38.49
2100	42.99	42.52	29.31	27.42

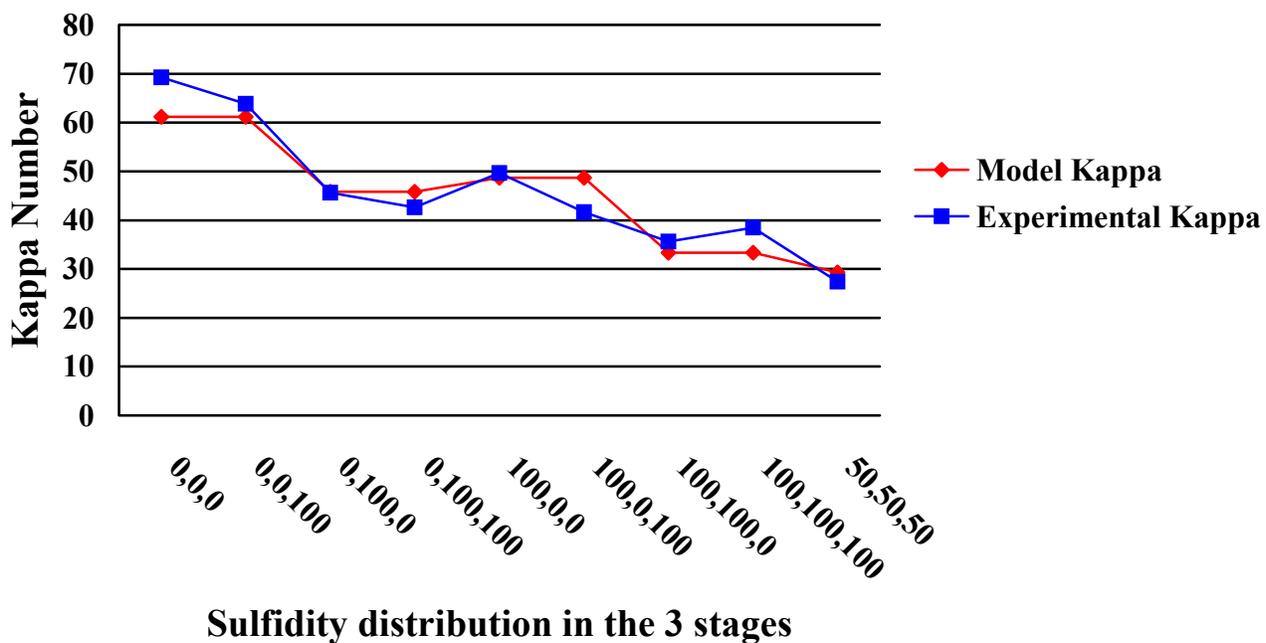


Figure A: Model and Experimental Kappa Number (H-Factor 2100)

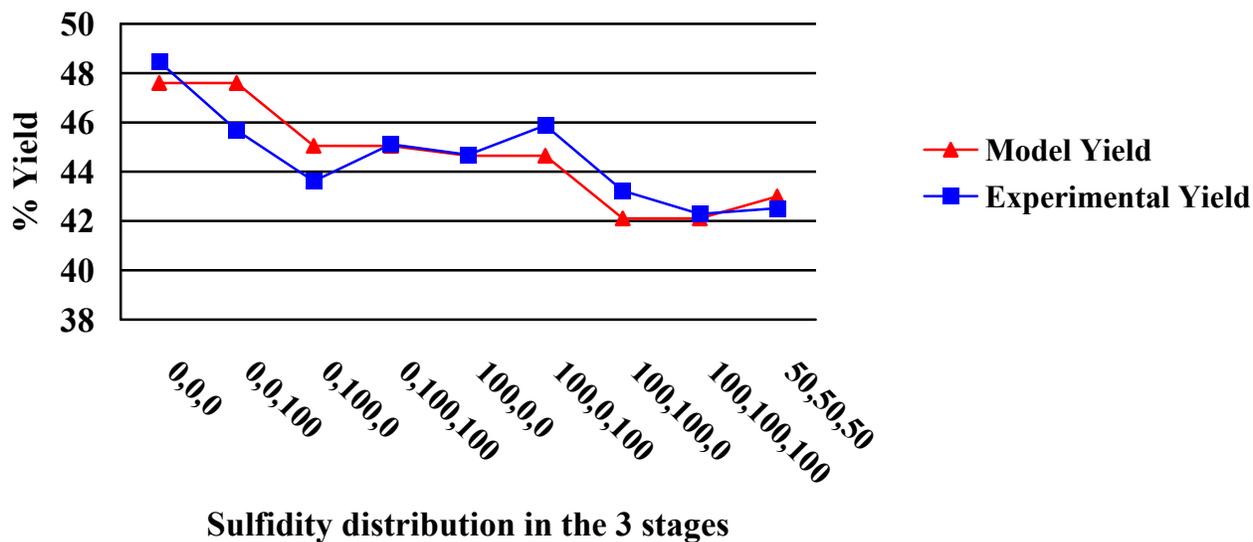


Figure B: Model and Experimental Yield (H-Factor 2100)

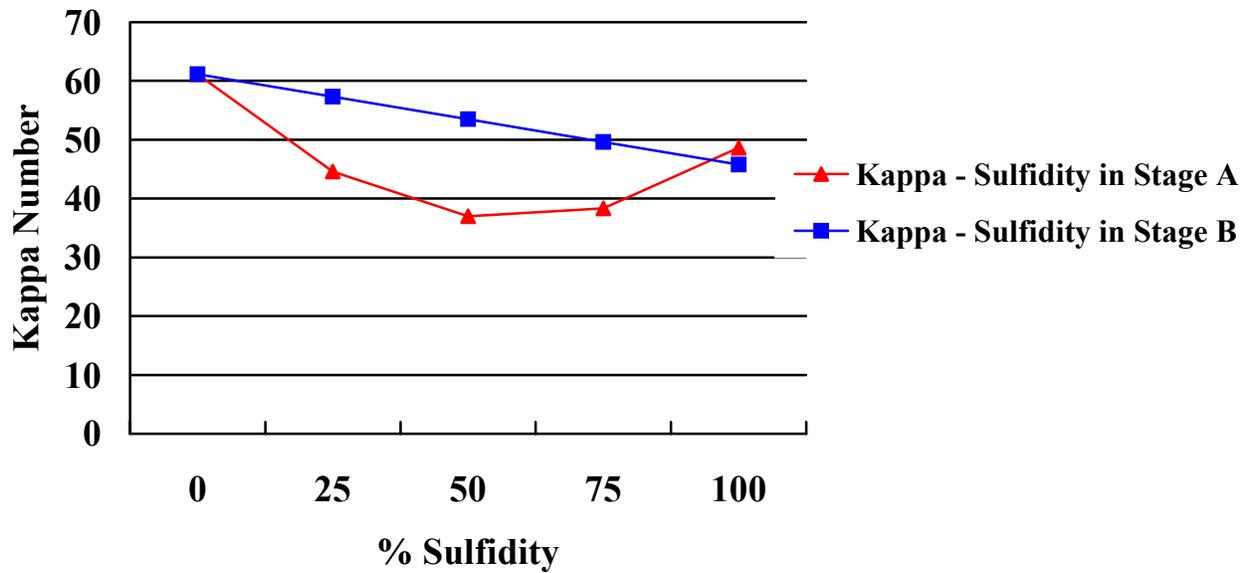


Figure C: Model Kappa Number Vs % Sulfidity in stages A and B (H-Factor 2100)

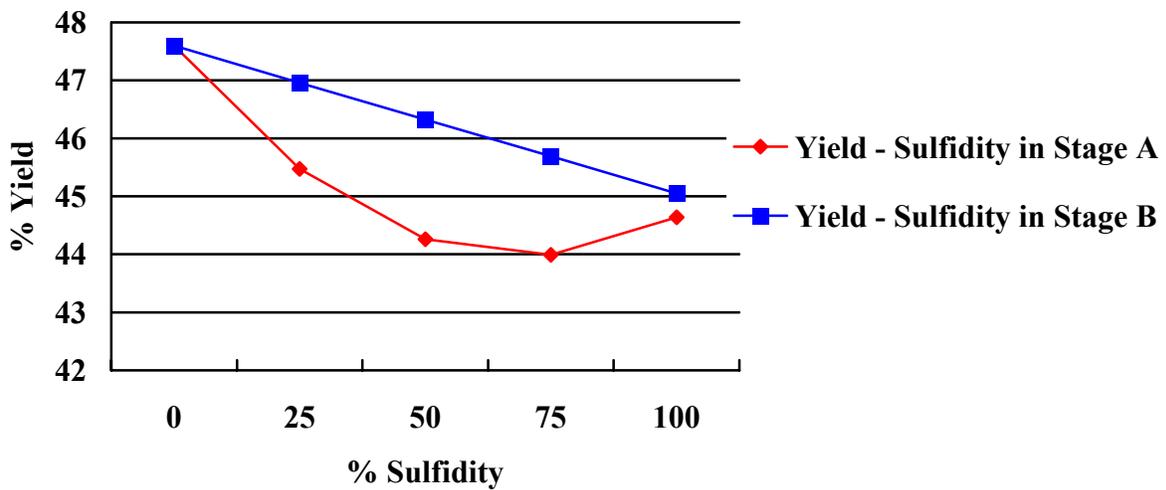


Figure D: Model Yield Vs % Sulfidity in stages A and B (H-Factor 2100)

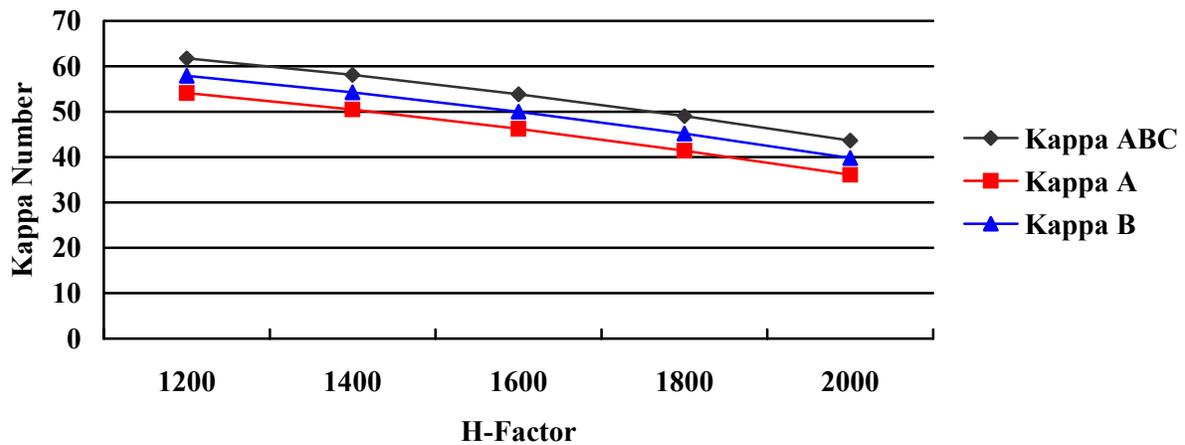


Figure E: Model Kappa Number Vs H-Factor

Kappa ABC – 25% sulfidity in all stages
 Kappa A – 50% sulfidity in A, 25% in B, C
 Kappa B – 50% sulfidity in B, 25% in A, C

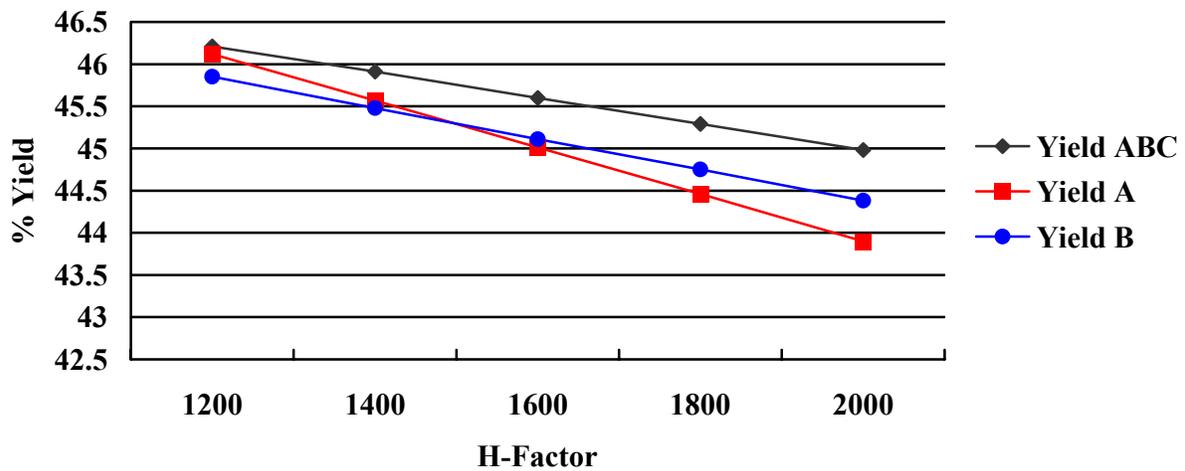


Figure F: Model Yield Vs H-Factor

Yield ABC – 25% sulfidity in all stages
 Yield A – 50% sulfidity in A, 25% in B, C
 Yield B – 50% sulfidity in B, 25% in A, C

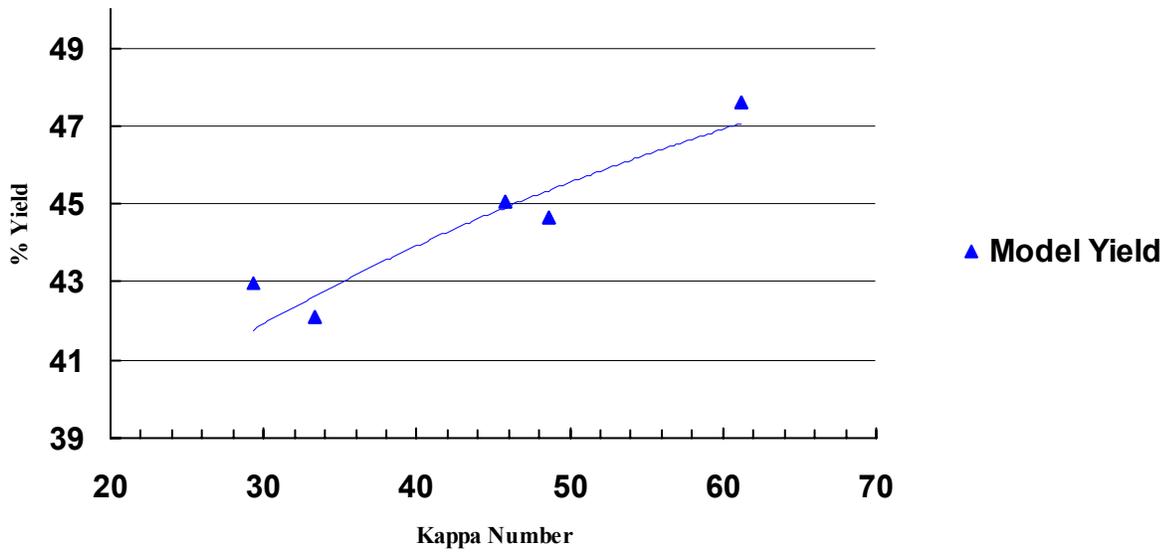


Figure G: Yield Vs Kappa Number (Model results, H-Factor 2100)

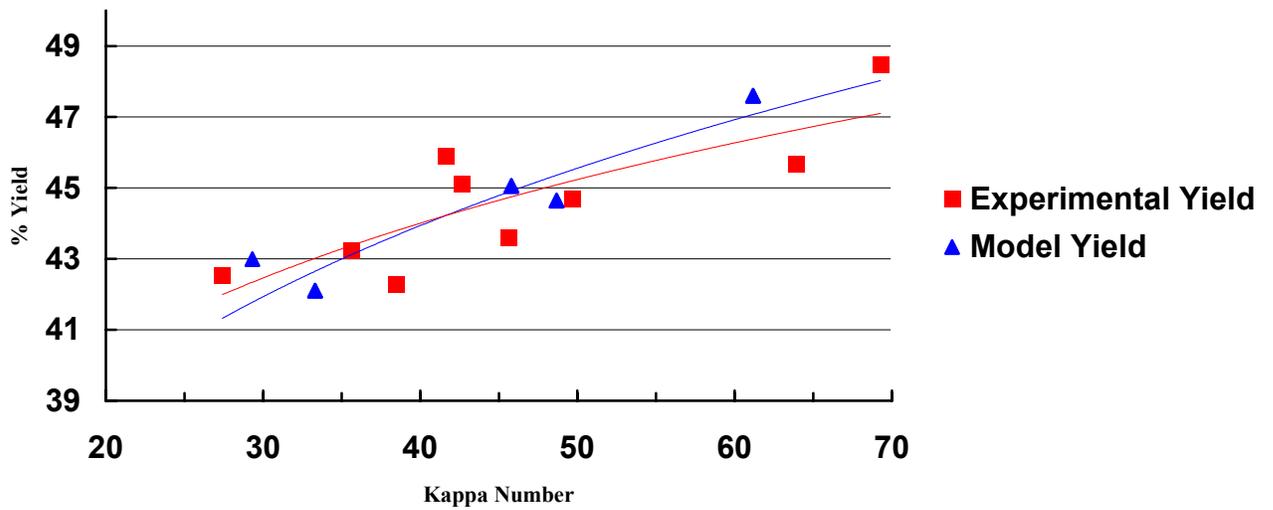


Figure H: Yield Vs Kappa Number (Experimental and Model results, H-Factor 2100)