

# CHALMERS



## **Decreased Wet Strength in Retorted Liquid Packaging Board**

*Master of Science thesis in the Master Degree Programme Materials and Nanotechnology*

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*Division of Organic chemistry*

CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden 2012

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Master of Science Thesis

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Cover:  
The Tetra Recart packaging.

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## ABSTRACT

The Tetra Recart is a retortable food packaging, suitable for high viscous products, making it able to replace most food cans used for storage of food today. The packaging is built up by a paperboard, consisting of an unbleached bottom layer and a bleached top layer. Polymers and aluminium further cover the paperboard in order to protect the food against moisture and light, causing degradation. During the retorting process, the packaging develops a certain wet strength making it hard to disintegrate the pulp fibres in the board. The phenomenon of the developed wet strength is of high interest when inventing and developing new packaging materials.

To investigate why and how the phenomenon occurs, a series of trials were made through production of laboratory sheets with subsequent disintegration. The addition and amount of cationic starch was varied as well as the addition of alkyl ketene dimers, AKD, to investigate their influence on the developed wet strength. A hemicellulose or a cellulose derivative was adsorbed on the pulp fibres in order to see if the phenomenon could be prevented and thereby explained. Two types of lignin was also adsorbed on the pulp fibres to evaluate the influence of lignin on the phenomenon. Finally, the Klason lignin content in the non-retorted and retorted paperboard was measured to investigate a possible change in the chemical composition of lignin.

Results showed that the addition and amount of cationic starch as well as the addition of AKD has an effect on the developed wet strength. Adsorption of a hemicellulose or a cellulose derivative on the pulp fibres can be used to prevent the phenomenon to occur. Adsorption of a lignin on the pulp fibres cannot be used to evaluate its influence on the phenomenon. Instead, adsorption of a lignin prevents the phenomenon to occur in the same way as a hemicellulose or a cellulose derivative. Measurements of the Klason lignin content showed a decrease in Klason lignin when retorting the paperboard for 1 hour but an increase in Klason lignin again when retorting the paperboard for 1.5 hour and 2 hours.

Keywords: Liquid packaging board, wet strength, retorting, cationic starch, AKD, lignin.



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# 1. INTRODUCTION

## 1.1 Background

Korsnäs is a pulp and paper company producing different types of packaging paper. The company has four packaging areas; liquid packaging, cartonboard, white top kraftliner and sack and kraft paper, all produced from virgin fibre (Korsnäs, 2011). There are three mills within Korsnäs; Gävle that is producing kraft pulp, paper and board, Frövi that is producing kraft pulp and board and Rockhammar that only produces CTMP-pulp<sup>1</sup>.

There are high demands on liquid packaging board since it is used for storage and transport of liquids and food. The most important is of course that the board is hygienic and that it does not transfer any smell or taste to the content. The stability of the packaging is also of great importance when transported and that the packaging is easy to grip when being used.

Tetra Pak is the largest company within the food processing and packaging industry (TetraPak, 2011). There are Tetra Pak sites all over the world developing and producing suitable and functional packaging for the different demands in different countries. Tetra Pak is a part of the Tetra Laval group, which has its headquarters in Switzerland.

Tetra Pak generates solutions for both liquid and food packaging to be able to preserve their hygiene and functionality. One of their packaging and processing systems is the Tetra Recart<sup>2</sup> system, a retortable carton packaging that can be filled with particulates and high viscous food products. Opposite to the traditional aseptic systems, the Tetra Recart packaging is sterilized together with its content in a cooking vessel (retort, or pasteur tunnel) (TetraPak, 2011). When using this type of sterilization process the food stays fresh for up to 24 months. Since the conditions in the cooking vessel can be very tough in terms of moisture and heat (up to 130°C, 100% moisture for 1-3 hours), the demands of the paperboard are extremely high and a special designed board has been developed together with Korsnäs for the specific Tetra Recart system.

Today, Korsnäs produce the liquid packaging board used for Tetra Recart. The board is built up by a bleached top layer, for good printing properties, and an unbleached bottom layer. During retorting, above certain temperatures, the unbleached layer develops a wet strength known to be thermoinduced. The wet strength makes the retorted material more difficult to disintegrate compared to non-processed material or material processed at lower temperatures. The cause of the thermoinduced wet strength is not fully known but several theories exist.

The literature describes a covalent bond, occurring by auto-oxidation, between the cellulose chains as a possible reason for the increased wet strength after retorting (Back, 1967). Laboratory studies at Korsnäs have shown a connection between high lignin content and increased wet strength and that the wet strength is higher for unbleached pulp than for bleached pulp. There has also been shown that addition of the sizing agent AKD gives an increased wet strength for both unbleached and bleached pulp.

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<sup>1</sup> CTMP – Chemithermomechanical pulp

<sup>2</sup> Recart – Retortable carton

## **1.2 Purpose**

The aim of the project is to investigate the phenomenon of the developed wet strength during retorting and to try to find a way of preventing the phenomenon. The prevention shall be done through fibre modifications or addition of chemicals in order to produce an unbleached board, more easily disintegrated than the unbleached reference board after retorting.

The thesis will consist of a literature study where the theoretical reason for the difficult disintegration is discussed, laboratory work with fibre modifications or chemical additions and production of laboratory sheets. The laboratory sheets will be retorted, evaluated and compared in terms of disintegration revolutions against the unbleached reference sheet.

## **1.3 Limitations**

Terms and limitations of the project is that the chemicals used shall be food safety approved and the cost of the solutions shall be economically feasible.

## **1.4 Specification of question formulation**

- Why does the wet strength occur during retorting?
- What is the chemical definition of the phenomenon?
- How can the wet strength be decreased or prevented?

## 2. THEORY

### 2.1 Wood and wood fibres

Paper and its different paper grades are built up by fibres originating from wood. Wood is divided into coniferous and deciduous trees, also called softwood (SW) and hardwood (HW) (Daniel, 2004). There are some significant differences between the different wood fibres giving them a wide variety of properties.

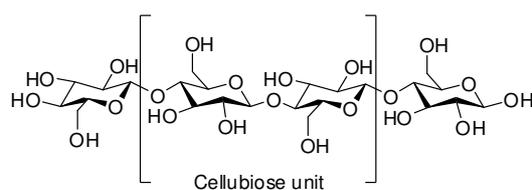
Softwood fibres generally consist of long and slender tracheid cell with a typical length of 2-4 mm and a diameter of 20-40  $\mu\text{m}$  (Brelid, 2009). Tracheid cells main purpose is to give the tree mechanical strength and to transport liquid (Brelid, 2009). A small amount of the fibres are ray parenchyma cells that are very much similar to tracheid cells but shorter and thinner (Daniel, 2004). Their main function is to store nutrients (Brelid, 2009).

Compared to softwood fibres, hardwood fibres have a much more complex morphology. Besides tracheids, including libriform cells, and ray parenchyma cells hardwood fibres also have vessels. The vessels have a dimension of 0.3-0.6 mm in length and 30-130  $\mu\text{m}$  in diameter and are linked together forming longitudinal tubes (Brelid, 2009). Their tube like appearance make them specialized in transportation of fluid and gives hardwood a porous structure (Daniel, 2004). The libriform cells have a length of 0.8-1.6 mm and the fibre tracheids 0.5-0.8 mm (Brelid, 2009). Both have a diameter of 14-40  $\mu\text{m}$  and have almost no participation in the transportation of liquid but focus on giving the tree mechanical strength (Brelid, 2009). As in softwood, the function of the ray parenchyma cells is to provide storage of nutrients.

Depending of what type of properties the paper is to have different fibres is used. Softwood fibres are longer and thinner than hardwood fibres and will therefore form a larger network where the fibres cross and lock each other on several places (Brelid, 2010b). This will provide strength to the paper but also make it less flexible due to more internal bonding between the fibres. The shorter hardwood fibres gives excellent formation of the paper since the fibres do not aggregates to the same extent as for long softwood fibres and thereby form a more open structure (Brännvall, 2004). This makes the paper smooth and flexible but also weaker since the open structure will not have the same ability for internal bonding.

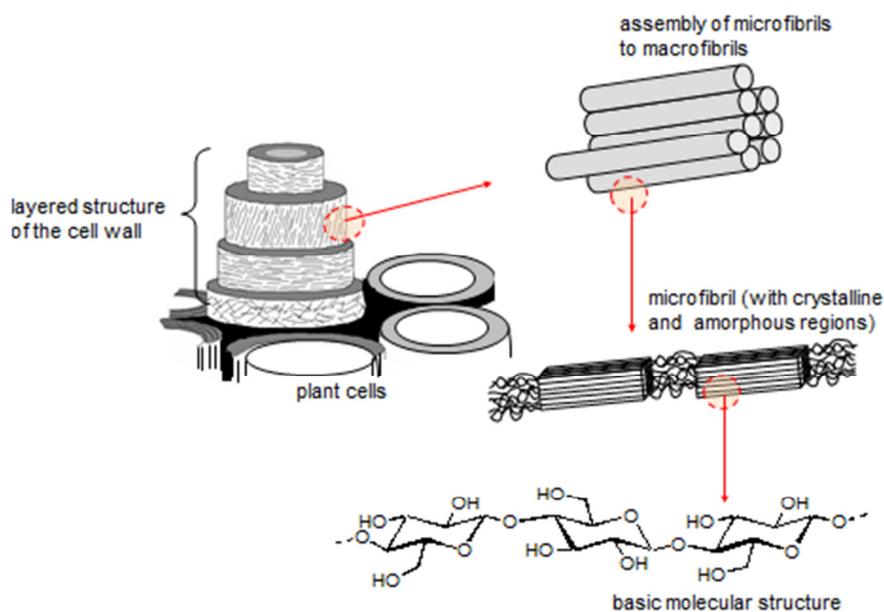
### 2.2 Cellulose

Cellulose is the main component in the natural material wood. Together with hemicellulose and lignin it forms a matrix with a complex structure called a wood cell (Daniel, 2004). Depending on the type of wood, the cells look different in chemical composition and distribution of cellulose, hemicellulose and lignin (Daniel, 2004). The cells are built up by a cell wall, which consists of several layers, where cellulose is the crystalline part giving the structure of the cell wall. Cellulose is built up by  $\beta$ -D-glucose units covalently linked together by  $\beta$ -1,4 glucosidic bonds into a polymer chain. The repeating unit of two glucose monomers is called cellobiose.



*Figure 2-1 Polymer chain structure of cellulose.*

Wood cellulose has a degree of polymerization of about 8,000 compared to cotton cellulose that has a degree of polymerization of about 10,000 (Lennholm and Blomqvist, 2004). The chains align next to each other and bind together through hydrogen bonding between hydroxy groups positioned along the chain (Lennholm and Blomqvist, 2004). The ordered chains give rise to a sheet structure that is layered on top of another sheet creating a three-dimensional structure held together by van der Waals bonds and hydrophobic interactions (Lennholm and Blomqvist, 2004). This three-dimensional structure gives cellulose microfibrils that are further aggregated into macrofibrils, part of the different layers in the cell wall (Daniel, 2004). Hemicellulose is then connected to the cellulose macrofibrils generating an amorphous structure in between. Lignin, which is amorphous and isotropic, further embeds the cellulose-hemicellulose structure and binds the whole matrix together (Daniel, 2004).



*Figure 2-2 Structure of cellulose in a wood cell (Hasani, 2010).*

During production of chemical pulp from wood, wood chips are cooked in cooking chemicals (sodium hydroxide and sodium sulphide) separating the fibres from each other and ending up

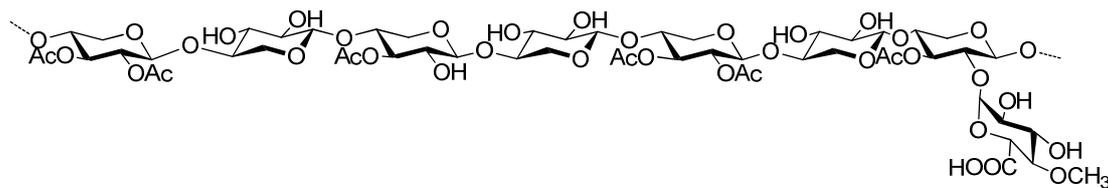
as negatively charged. The cooking chemicals degrade both hemicelluloses and lignin and change the structure of the cellulose microfibrils. The cellulose microfibrils will come closer together and get a more dense structure to form larger aggregates (Lennholm and Blomqvist, 2004). The large formed aggregates will be of great importance for the fibre properties due to changes in the cell wall structure.

## 2.3 Hemicellulose – Xylan

Hemicelluloses are a group of heteropolysaccharides, compared to cellulose which is homopolysaccharides, existing in plants. They are built up by hexoses and pentoses and have different compositions depending on what type of plant they originate from (Teleman, 2004). Hemicelluloses have a degree of polymerization of about 100-200 (Brelid, 2009) and are structural carbohydrates as they are a part of the cell wall together with cellulose and lignin. The biological function of hemicelluloses is not fully clear but there are many suggestions where they contribute to the mechanical properties of the cell wall and that they have good ability to store water (Teleman, 2004).

Softwood and hardwood trees have different types of hemicelluloses. The most common hemicellulose in softwood is glucomannan, in the presence of 10-15%, which consist of  $\alpha$ -D-galactopyranosyl units linked to mannose.

The most common hemicellulose in hardwood is glucuronoxylan, in the presence of 15-35%, which is built up by xylopyranosyl units with 4-*O*-methyl-glucuronic acid and *O*-acetyl as side groups. It is commonly occurring that the units carrying a 4-*O*-methyl-glucuronic acid also carry an *O*-acetyl group (Teleman, 2004).



*Figure 2-3 Molecular structure of glucuronoxylan, hardwood xylan, with xylopyranosyl as backbone and 4-*O*-methylglucuronic acid and *O*-acetyl as side groups.*

There is also softwood xylan, in the presence of 7-15%, with the only difference of an L-arabinose as side group instead of *O*-acetyl (Teleman, 2004).

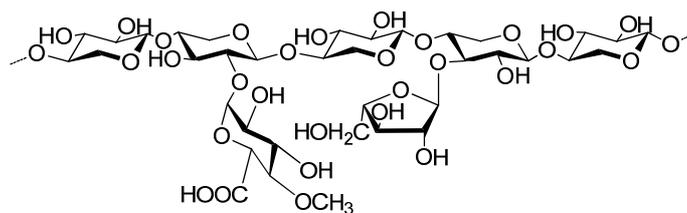


Figure 2-4 Molecular structure of arabino-4-O-methylglucuronoxylan, softwood xylan, with xylopyranosyl as backbone and 4-O-methylglucuronic acid and L-arabinose as side groups.

Due to its irregular side groups, 4-O-methylglucuronic acid and O-acetyl, xylan is amorphous which provides high accessibility in the cell wall and makes it reactive (Brelid, 2009).

## 2.4 Lignin

Lignin is one of the most common biopolymers and creates together with cellulose a type of microcomposite material where cellulose acts as reinforcing fibres and lignin as a phenolic plastic (Henriksson, 2004). Lignin is built up by a mixture of aromatic and aliphatic constituents and has a three-dimensional structure linked together by ether- and carbon-carbon bonds. The aromatic constituents consist of three main monomers; *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Henriksson, 2004).

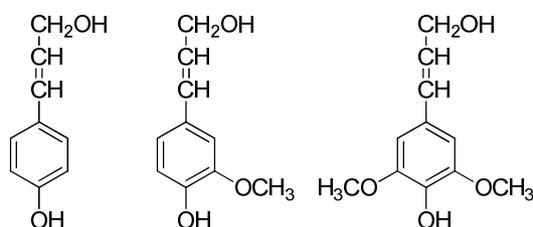


Figure 2-5 *p*-Coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

There are three different types of lignin; hardwood lignin, softwood lignin and grass lignin. Hardwood contains about 15-35% lignin and has a much more complex lignin structure than softwood, which consists of about 20% lignin.

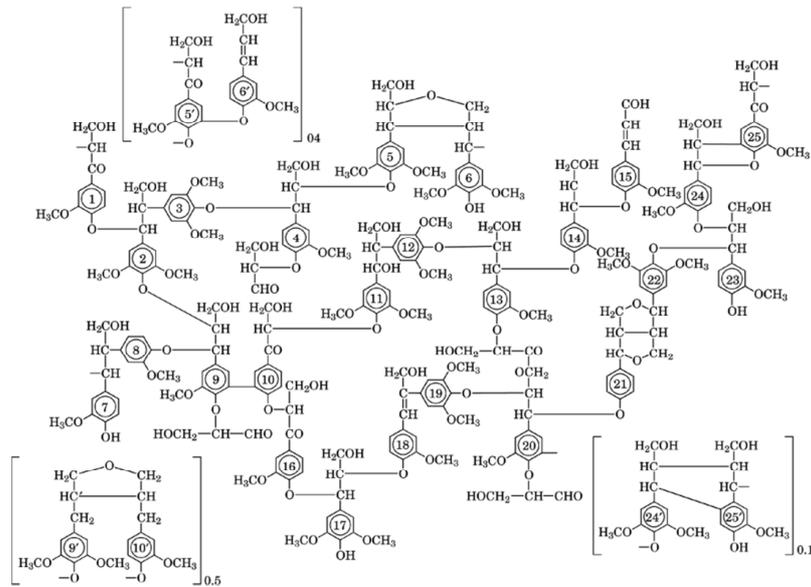


Figure 2-6 Structural suggestion of lignin in beech, HW (Lebo et al., 2001).

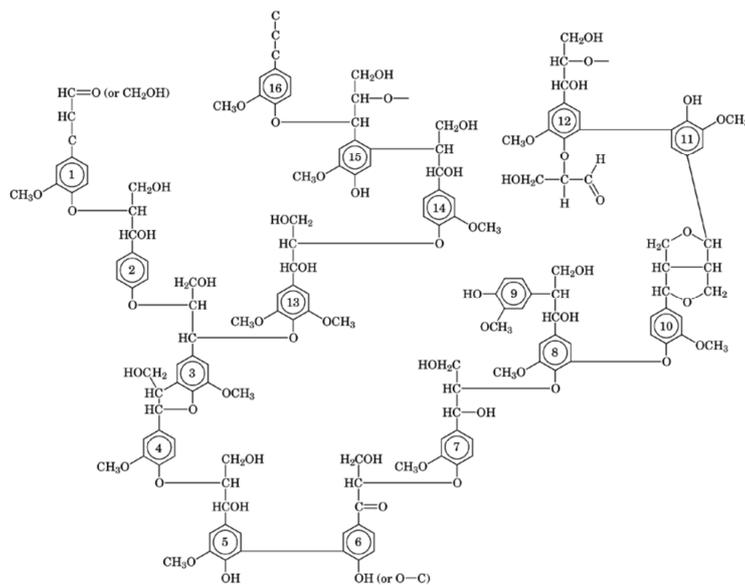


Figure 2-7 Structural suggestion of lignin in spruce, SW (Lebo et al., 2001).

Lignin is believed to be located all through the cell wall, embedding the cellulose and hemicellulose structure, and to a high extent in the middle lamella (Henriksson, 2004). When embedding the polysaccharides, lignin provides stiffness to the cell wall that gives good mechanical properties. The lignin rich middle lamella acts as glue, keeping the different wood cell together. Lignin also makes the cell walls hydrophobic and prevents it from swelling which is important since the cells need to transport water and nutrients through the wood stem (Henriksson, 2004). The last important function of lignin is its protection against microbial degradation of wood where it surrounds the polysaccharides so close that no degrading microorganism proteins are able to penetrate into the cell wall (Henriksson, 2004).

### *Lignin measurements*

Amount of lignin present in a pulp sample is determined through acid hydrolysis. The acid hydrolysis results in a solution of monomeric sugars and lignin kept as a precipitation, called the Klason lignin. The precipitation is weighed and the lignin content is determined gravimetrically.

To determine the chemical composition of lignin, several kinds of chemical treatments can be used dependant on what type of information is to be looked for about the lignin. Oxidation of lignin can be used to determine the amount of methoxy and hydroxy groups on lignin monomers and through NMR<sup>3</sup> analysis it is possible to get a hint of how the monomers are linked together in the large network.

### *Kappa number*

Determination of Kappa number is an analytical method, which describes the amount of lignin still present in a pulp after chemical pulping (Gellerstedt, 2004). The method is based on calculating the content of oxidizable groups in a pulp, which mainly is seated on lignin, through excess addition of acidic potassium permanganate. The kappa number gives an indication of how far the delignification of the fibres has proceeded.

### *The phenomenon auto-adhesion*

Production of fibreboards, particle boards and paper boards uses a technique where bonding of wood fibres or particles is generated through high pressure and temperature. The phenomenon is called auto-adhesion and based on the formation of radicals when oxidizing lignin (Felby et al., 2004). The radicals further react with other wood components creating covalent bonds and a cross-linked structure. The cross-linked structure provides high wet strength and thereby a more stable material (Felby et al., 2004).

## **2.5 Starch**

Starch has the same structure as cellulose but is instead linked together by  $\alpha$ -1,4 glucosidic bonds. The starch polymer can appear as both linear and branched, called amylose and amylopectin (Clerck, 2009). The branching takes place at the 1,6-position on the glucose units. The linear polymer has a degree of polymerization of 1,000-4,000 glucose units whereas the branched polymer is one of the largest naturally occurring polymers and has a degree of polymerization of up to 4,000,000 glucose units (Clerck, 2009).

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<sup>3</sup> NMR – Nuclear Magnetic Resonance

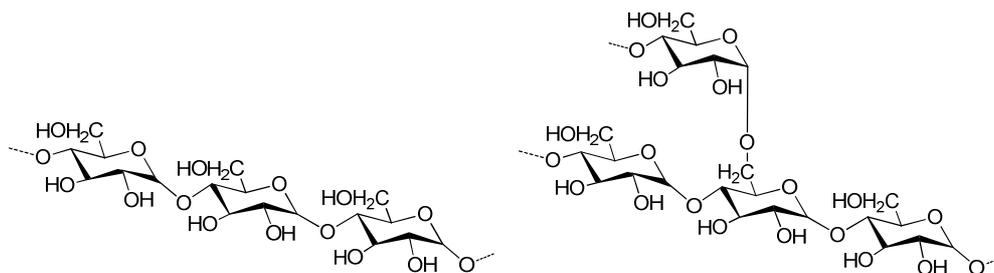


Figure 2-8 Starch as linear amylose and branched amylopectin.

Due to the similarity between cellulose and starch, the polymers have a substantial affinity towards each other. In order to get even higher affinity between cellulose and starch the starch is often cationized (Brelid, 2010a). The cationized starch will adsorb to the negatively charged fibre surface until all hydroxy groups are taken or until the surface charge is fully compensated (Clerck, 2009). The main function of starch addition is to increase the dry strength of the material but it has also a significant effect on the retention of fines and added chemicals in the pulp (Clerck, 2009).

## 2.6 Cellulose derivatives

Due to the three hydroxy groups on glucose, cellulose can be modified on a wide variety of ways (Zugenmaier, 2008). Modified cellulose is called cellulose derivatives and some common derivatives are carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC) and hydroxypropyl methylcellulose (HPMC). Hydroxypropyl methylcellulose phthalate (HPMC-P) is a version of HPMC but with phthalate as a side group as well making it less hydrophilic.

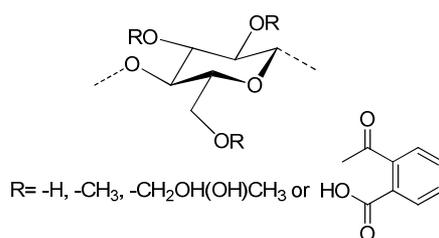


Figure 2-9 Chemical structure of cellulose derivatives.

The derivatives mentioned above have a specified solubility in different solvents why they are excellent to use in food applications as a thickener or stabilizer (Imeson, 2010) or in pharmaceuticals as a controlled drug delivery system (Roy et al., 2010).

## 2.7 Sizing and sizing agents

The main function of sizing agents is to prevent penetration or wetting by liquids of paper or paperboard products (Lindström, 2004). There are both surface sizing and internal sizing which acts in different ways. Surface sizing is done at the end of the paper web formation and is used to create a smooth and even surface with good printing properties (Lindström, 2004).

Internal sizing is used to control and decrease the liquid penetration into a paper structure by addition of hydrophobic substances which covalently binds to the fibres (Lindström, 2004). Sizing agents are not able to prevent vapour penetration through a paper, this only a physical barrier is able to. There are several mechanisms for liquid penetration of paper and two of the most important are referred to as inter-fibre penetration and intra-fibre penetration (Lindström, 2004). Inter-fibre penetration describes the process of penetration of liquid through the pores of a paper structure where capillary pressure is the driving force and liquid is transferred between the fibres. Intra-fibre penetration is described as diffusion of liquid through fibres, making them swell. Penetration through the pores breaks the hydrogen bonds between the fibres creating changes in the paper structure. The same event happens in the fibre swelling process.

A sizing agent must be reactive to both cellulose and water and the balance between these are very important. Addition of a sizing agent is mostly done through an emulsion or dispersion. When a sizing agent reacts with cellulose it covalently links to the fibre, getting high orientation with its long hydrophobic tail pointing outward from the fibre. Due to the high orientation and disability to move, generated by the covalent linkage to the fibre, sizing arises at very low levels.

### *AKD*

One of the most common sizing agents is alkyl ketene dimers, AKD, invented during the 40's. AKD consist of a lactone ring, which is reactive towards the hydroxy groups present in cellulose forming a  $\beta$ -keto ester. The lactone ring is also reactive towards water and gives a  $\beta$ -keto acid which instantly decarboxylates into the corresponding ketone, unable to react with cellulose. The reaction towards cellulose is slow and although both reaction and hydrolysis occurs, the reaction towards cellulose is stronger than the hydrolysis and AKD works as an effective sizing agent.

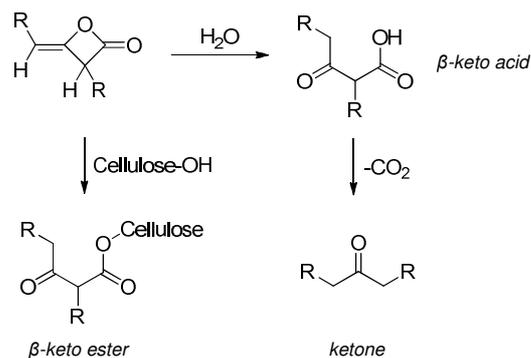


Figure 2-10 Reaction and hydrolysis of AKD (Lindström and Larsson, 2008).

To speed up the reactivity towards cellulose, different accelerators can be added. The addition of an accelerator can increase the rate of reaction by an order of magnitude. Commonly used accelerators are bicarbonate,  $\text{HCO}_3^-$ , and basic polymers with amine groups, both having a free electron pair.

#### ASA

Another common sizing agent nowadays is alkenyl succinic anhydride, ASA. Just like AKD, ASA can react with cellulose and give the fibres a more hydrophobic surface (Lindström, 2004). ASA is made from 1-alkenes or  $\alpha$ -olefins that are catalytically isomerized and further reacted with maleic anhydride. ASA is much more reactive towards cellulose but will also undergo hydrolysis much faster why ASA is prepared at the paper mill and added close to the web formation in the paper making procedure (Brelid, 2010a).

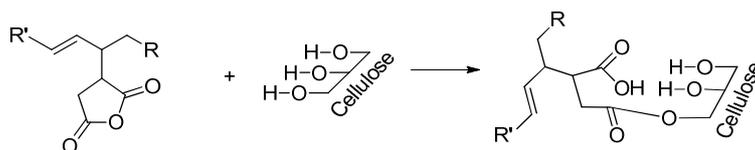


Figure 2-11 Reaction of ASA with cellulose (Lindström, 2004).

## 2.8 IR spectroscopy

Infrared spectroscopy is a qualitative analysis method especially suitable for detection of carbonyl compounds. The infrared region, used for analysis of organic compounds, occurs between  $2.5 \times 10^{-5}$  and  $2.5 \times 10^{-6}$  cm (Lampman et al., 2010). The method uses the vibration energy of different bonds when exposed to infrared light to separate different functional groups within the molecule. When a molecule is hit by a frequency matching its bond energy, the energy is absorbed and stretching and compressing of the bond between the atoms can increase a bit more (Lampman et al., 2010). The absorbed energy gives rise to a peak in a spectrum that further can be analysed by looking at frequencies for known functional groups.

There are several types of vibrations depending on the structure of the molecule. Stretching is one type of vibration and can be both symmetric and asymmetric. Another type of vibration is bending which is divided into out-of-plane bending, called wagging and twisting, and in-plane bending, called scissoring and rocking (Lampman et al., 2010).

Carbonyl compounds have a strong dipole moment, which gives them very characteristic frequencies that always are the same in an IR spectrum. The absorption of an aldehyde occurs as a strong narrow peak around 1740-1690  $\text{cm}^{-1}$  and for O-H-groups as a strong broad peak around 3550-3200  $\text{cm}^{-1}$  (Webspectra, 2000).

## 2.9 Food and liquid food packaging

Packaging's used for storage of food have high demands since they are to be in contact with food. Three major functions of food and liquid food packaging are:

- 1) Protection of the content
- 2) Distribution and handling
- 3) Information and marketing

The main function is to protect the food and thereby prevent food waste. The package must therefore be hygienically produced and filled or treated. It is important that the packaging do not affect the food in case of flavour and taste and that it is stable and stiff to fulfil both functional and mechanical properties (Korsnäs, 2011). The content is also protected when the packaging is designed to provide sufficient shelf life and as easy to empty.

When considering transportation and distribution of the product, the weight and the geometrical shape of the packaging is of great importance to make it as efficient as possible (Berg, 2012). Stability and stiffness is needed in order to fulfil logistic requirements and avoid damages during transportation.

The packaging is a way for the producer to profile the company and the brand making the printing properties significant. The packaging should visualize pictures and text providing information from the producer regarding the content, how to open the packaging and how to dispose the packaging. It should also attract consumers' interest once displayed on the shelf in a grocery store.

Except for these three main functions of the packaging, there are other requirements for packaging producers to consider, such as environmental performance, packaging sizes and consuming trends (Berg, 2012).

## 2.10 Liquid packaging board

There are many types of paperboard grades mainly divided into three classifications namely carton boards, containerboards and specialty boards (Lindberg, 2000). Common for most

paperboards are a basis weight higher than 150 g/m<sup>2</sup> and multi-ply structure to achieve good strength properties.

Liquid packaging board is used, as described above, for storage and protection of food and liquid food creating high demands on the board production. Only virgin fibres can be used to insure the purity and cleanliness of the board (Lindberg, 2000). Depending on the forthcoming content of the package the board is produced in different ways. To be able to achieve high stiffness of the package the board is produced with several layers withholding altered properties. In a two-ply board, the bottom layer usually consists of pulp with high bulk providing lower basis weight for a given stiffness (Lindberg, 2000). The top layer is made from pulp with a high modulus of elasticity. The multi-layer structure makes the formation of the board quite complicated. Depending on number of layers in the board, the machines are designed differently. One example is to form the top layer first and then apply middle plies and back layer on top of the top layer. The different layers are produced by spraying a pulp and water mixture out from several headboxes onto fourdriniers where the pulp is dewatered and later merge the layers together in a press section usually consisting of a shoe press. The press section provides maximum bulk, as the board reaches wanted dryness (Lindberg, 2000). The board then enters a drying section to achieve full dryness. If the board is to be printed on with high-quality prints, a coating can be applied at the end of the machine. The board is finally calendered to get high smoothness.

#### *Retortable board*

The liquid packaging board produced at Korsnäs has a grammage of 240 g/m<sup>2</sup> is built up by two layers. One bottom layer made out of unbleached softwood pulp and broke and one top layer which is made out of bleached hardwood pulp and bleached softwood pulp (Tufvesson, 2007). The board has a density of 750 kg/m<sup>3</sup> and is sized with AKD.

#### *Board process*

The stock, both HC<sup>4</sup>- and LC<sup>5</sup>-refined, is diluted and mixed with paper chemicals e.g. retention aid, dry strength chemical, sizing agent and fillers. The fibre suspension, with a concentration of less than 0.2% in the headbox, is sprayed out on the wire where the paper web immediately is formed through dewatering of the fibre suspension. The two layers are couched together in a press on the wire section, which gives the board a dryness of approximately 20% (Tufvesson, 2011). After the press section, the paper has a dryness of approximately 40% and enters the drying section where the web is dried on drying cylinders. The drying cylinders are heated with steam supplied from the recovery boiler at the plant. The drying is energy demanding and the dryness increases to 90% (Tufvesson, 2011).

## **2.11 Sterilization**

In order to keep food fresh for a longer period of time, microscopic organisms within the product must be degraded. The degradation is done thermally, which generates an

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<sup>4</sup> HC – High Consistency

<sup>5</sup> LC – Low Consistency

environment where spoilage-type microorganisms and their spores cannot grow. Only anaerobic microorganisms are of concern since the packaging lack of oxygen. The anaerobic microorganisms are pH-dependent and can thereby be divided into three different types of food groups; high acid food, acid food and low acid food (Holmgren, 2005). Many microorganisms cannot survive in a very acid environment and the food product will not demand such severe sterilization. The critical group is the low acid food where the survival and multiplication of microorganisms are high and a more extreme sterilization of the food must be performed (Holmgren, 2005).

*Clostridium botulinum* is the most aggressive microorganism in low acid food and very important to control since it produces botulinum toxin (Holmgren, 2005). The toxin causes botulism which is a muscle and respiratory paralyzing condition and direct lethal (Holmgren, 2005).

The heating of food products leads to undesirable degradation of nutrients such as vitamins, making it important to optimize the sterilization process in order to maintain quality factors and still produce safe food (Holmgren, 2005).

Most of Tetra Pak's liquid food products are processed aseptic. Aseptic processing and packaging is based on a heat-hold-chill process where a product, in a continuous flow, is filled and sealed in a commercially sterile package and environment.

If a food product contains too large particles, aseptic processing is no longer possible. The Tetra Recart packaging may sometime contain vegetables, beans or pet food and must therefore be sterilized in a different way, called retorting or pasteurization. The significant difference is that the product is filled and sealed in an unsterile packaging and environment. The product and packaging is thereafter sterilized together in a retort chamber or a pasteur tunnel (cooking vessel).

Pasteurization is a milder sterilization process for high acid food e.g. tomatoes where the temperature is kept at maximum 95°C.

### *Retorting*

Retorting is built up by four stages: loading, heating, cooking and cooling. In the first step the packaging is filled with food and sealed without presence of air. The packaging is then put into a rack, which improves the heat transport through the packaging, and subsequently put into a retort that is pressurized and heated up to a set temperature using steam, steam/air or other heat transport mediums. When having flexible packaging, the internal pressure inside the packaging will be become large during retorting and a risk of collapse occurs (Holmgren, 2005). The retort will therefore have an overpressure to be able to stabilize and keep the packaging in their original shape. The temperature is in general between 110°C and 130°C and the time is defined upon the characteristics of the food processed (Holmgren, 2005). After the finished sterilization period, the packaging is cooled down through replacing the steam with compressed air to avoid collapse of the packaging due to the thermal pressure inside. When the pressure is stabilized, it continuous to be released stepwise and the packaging is further cooled down to their end temperature using spray-cooling.

## 3. MATERIALS AND METHODS

### 3.1 Pulps and chemicals

Softwood and hardwood pulp was taken out from Korsnäs mill in Gävle with a kappa number of ~55 respectively ~17. The hardwood pulp has a much lower kappa number because its fibres will not separate from each other at higher kappa numbers. Fully bleached hardwood and softwood pulp was taken out from Korsnäs mill in Frövi. Below, chemicals used in the trials are shown.

*Table 3-1 Chemicals used in the trials.*

Chemical	Supplier	Item number	Batch number
NaHCO <sub>3</sub>	Merck	Laboratory chemical	
Alum (AlSO <sub>2</sub> )	Merck	Laboratory chemical	
Cationic potato starch		Amylofax	
Alkyl ketene dimer, AKD	Eka	DR 28HF	
Silica sol, BMA	Nalco	8699	
Xylan	Sigma-Aldrich	X4252	212331
Hydroxypropyl cellulose, HPC	Hercules Incorporate, Ashland	Klucel hydroxypropyl cellulose	
Hydroxypropyl methylcellulose, HPMC	Shin-Etsu Chemical Co.	Metolose 60SH-50	
Hydroxypropyl methylcellulose phthalate, HPMC-P	(Astra Zeneca)		
Lignin, alkali	Sigma-Aldrich	471003	
2,6-Di-tert-butyl-3-methylphenol (antioxidant)	Sigma-Aldrich	B1378	

### 3.2 Modification of lignin

Lignin with low sulfonate content was bought from Sigma-Aldrich and methylated at Chalmers according to previous literature protocols (Brodin et al., 2010). The methylation was successful shown in the IR-spectrum, Figure 3-1, where the broad O-H-peak has decreased significantly and been replaced by methoxy groups seen below 3000 cm<sup>-1</sup>.

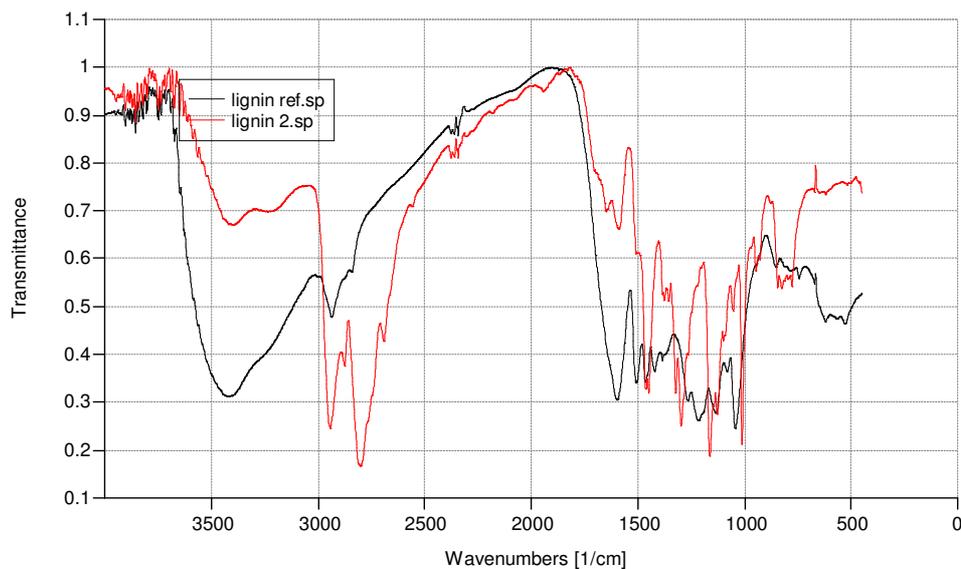


Figure 3-1 IR-spectrum of purchased reference lignin (lignin ref) and methylated lignin (lignin 2).

### 3.3 Production of laboratory sheets

A pulp mixture was prepared in an agitator containing pulp and deionized water and pH was adjusted to 7.7. Sodium bicarbonate, 5 kg/t, was added and pH was adjusted to 7.7 again, then alum, 3.0 kg/t, was added and pH was once again adjusted to 7.7. For one sheet of 4.4 g, 1.46 litre of the mixture, with the concentration of 0.3% which equals 3.0 g pulp/litre mixture, was needed. Cationic starch, 7.5 kg/t, was added to the 1.46 litre mixture and reacted for 30 seconds, then AKD, 4 kg/t, was added and reacted for 30 seconds and the mixture was then poured into a sheet former. Silicasol BMA, 0.5 kg/t, was added during agitation to the sheet former 5 seconds before dewatering. Sheets were produced in 1-ply with grammage of 140 g/m<sup>2</sup>, which equals 4.4 g/sheet, in a sheet former from Rapid Köthen.

The sheets were then pressed and dried in the Rapid Köthen for 12 minutes until dry. After the sheet production the sheets were cured in an oven at 105°C for 20 minutes.

#### *Reference sheets*

Reference sheets of unbleached and bleached pulp were produced according to above.

#### *Variation of starch addition*

Different amounts of starch (S3, S7.5, S10, S15, S20 kg/t) were added to the sheets of unbleached pulp in order to evaluate the effect on disintegration before and after retorting.

#### *Addition of xylan*

Sheets of unbleached pulp were produced with addition of 320 mg/g pulp xylan, during agitation for 3 hours, to evaluate its influence on disintegration during retorting (Köhnke and Gatenholm, 2007).

#### *Addition of HPC*

Sheets of unbleached pulp were produced with addition of 320 mg/g pulp hydroxypropyl cellulose (HPC), during agitation for 3 hours, to investigate if similar effects could be reached as for xylan during retorting.

#### *Addition of HPMC*

Sheets of unbleached pulp were produced with addition of 320 mg/g pulp hydroxypropyl methylcellulose (HPMC), during agitation for 3 hours, to investigate if similar effects could be reached as for xylan during retorting.

#### *Addition of HPMC-P*

Sheets of unbleached pulp were produced with addition of 320 mg/g pulp hydroxypropyl methylcellulose phthalate (HPMC-P), during agitation for 3 hours, to investigate if similar effects could be reached as for xylan during retorting but with a less hydrophilic behaviour.

#### *Addition of lignin and modified lignin*

Sheets of fully bleached pulp were produced with addition of 7% lignin or modified lignin of the total amount dry pulp, during agitation for 3 hours. This to evaluate the effect of methoxy groups instead of hydroxy groups, which are believed to form radicals, on lignin when retorted. Noted should be mentioned that the modified lignin did not completely dissolve in the pulp mixture.

#### *Addition of antioxidant*

Sheets of unbleached pulp were produced with addition of 7% antioxidant of the total amount dry pulp, during agitation for 3 hours, to evaluate if an antioxidant can counteract formation of radicals, which are believed to be formed during retorting. Noted should be mentioned that the antioxidant did not completely dissolve in the pulp mixture.

### **3.4 Industrial retorting**

Tetra Recart packaging material was formed, water-filled and sealed at the Tetra Recart development site in Lund. The packaging, seen in Figure 3-2, were retorted at different temperatures, 96, 110 and 130°C, also this at Tetra Recart in Lund.



Figure 3-2 Tetra Recart packaging.

### 3.5 Laboratory retorting

Laboratory sheets were rolled up and put into a beaker. The autoclave, Certoclav-Tisch-Autoclav CV-EL, was filled with approximately 1 litre of deionized water and the beaker was immersed into the autoclave. The lid was then put on, locked and the autoclave was set to 125°C and started. When the temperature had risen to 100°C the valve was closed and the temperature increased to 125°C. At 125°C, time was set to 60 minutes and when finished the autoclave was turned off. After 30 minutes the autoclave were opened and samples taken out and set into an oven at 70°C for 24 hours to remove excess water.

#### *Laboratory retorting in N<sub>2</sub>-atmosphere*

The deionized water was bubbled with N<sub>2</sub> to remove all oxygen and poured into the autoclave as above. Before immersing the samples, the autoclave was heated to 100°C and subsequently filled with N<sub>2</sub> to replace the oxygen. The autoclave was once again heated to 100°C and the valve was closed as above. Further procedure continued as above.

### 3.6 IR-spectroscopy

When analysing the liquid packaging board by IR spectroscopy the board was grinded in a laboratory grinder for less than a minute. The fibres were then separated to some extent from each other, being able to be mixed with potassium bromide salt. When the sample was mixed with KBr the mixture was pressed into a tablet, which then was analysed in the IR-spectroscopy equipment, Perkin Elmer Spectrum one.

Since cellulose is hygroscopic<sup>6</sup> the IR spectrum will have a large water peak over the carbonyl compounds and the tablet must therefore be dried and analysed again to be able to see the carbonyl peak.

### 3.7 SEM - Scanning electron microscopy

Scanning electron microscopy pictures of the non-retorted and retorted material, both with and without addition of different chemicals, was order from Korsnäs Frövi to evaluate if any differences could be seen between the materials.

### 3.8 Disintegration

Disintegration was performed according to the standard developed at Korsnäs AB Gävle. Instead of a disintegrator, a blender from Bamix with two speeds, I=10 000 rpm and II=15 000 rpm, was used. The standard uses 20 grams of pulp but at Chalmers the method was scaled down to 2 grams of pulp.

The sheets were grated into piece of 25 mm×25 mm and soaked in 0.1 litre of room temperature deionized water for 5 min in a beaker. Subsequently 0.1 litre of deionised water was added and the blender was immersed into the beaker. The blender was then run for 30 seconds at speed I, which equals 5000 revolutions, and a teaspoon of the pulp/water mixture is put into a graduate cylinder and diluted to 100 mL. The sample was then visually evaluated with respect to fibre bundles. The procedure was repeated until no fibre bundles were present and the sample was completely disintegrated.

### 3.9 Klason lignin

Klason lignin is a gravimetical method used to determine the lignin content of pulp. The lignin is separated from cellulose and hemicellulose through an acid hydrolysis, giving solid lignin, which can be filtered of from the dissolved cellulose and hemicelluloses.

200 mg dried sample was placed in a 150 mL beaker and 3 mL H<sub>2</sub>SO<sub>4</sub> (72%) was added. The pulp was then kneaded with a glass rod to make sure the acid wets the whole sample. The beaker was then placed under vacuum for 15 minutes to let the acid impregnate the sample. A pre-hydrolysis was done by putting the beaker in a water bath holding 30°C for 60 minutes. After 60 minutes the beaker was taken out of the water bath and a lid of aluminium foil was put onto the beakers. The sealed beaker was then placed in an autoclave, set at 125°C for another 60 minutes at which the autoclave was turned off to let cool down to 80°C. At 80°C, the beaker was taken out of the autoclave and the solution was warm filtered through a dried and pre-weighed glass filter. The hydrolysate was kept for measurement of acid soluble lignin

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<sup>6</sup> Hygroscopic – a substance able to attract and hold water molecules from the surrounding environment

and carbohydrate analysis if wanted. The glass filter was subsequently put in an oven at 105°C for 2 hours and finally weighed to determine the Klason lignin content.

### 3.10 Acid soluble lignin

The hydrolysate, generated during the acid hydrolysis described above, contains a small amount of lignin soluble in acid. The amount of acid soluble lignin was determined by measuring the hydrolysate, diluted 10x, in an UV spectrometer (Specord 205, Analytik Jena) at 205 nm. The amount was then calculated from:

$$ASL[\%] = \frac{100 \times Abs}{k \times m} \quad \text{Equation 1 (SIKT, 2011)}$$

where      Abs = absorbance  
              k = 100  
              m = sample amount [g]

### 3.11 Carbohydrate analysis

The hydrolysate described above mostly contains of dissolved cellulose and hemicellulose, i.e. monomeric sugar units, and can be quantified by using GC, HPLC or CE<sup>7</sup>. In this case a HPLC is used.

The hydrolysate was transferred to a 100 mL volumetric flask containing 2 mL fucose solution (2000 mg/L) and diluted to 100 mL with deionized water. The fucose concentration was then 40 mg/L and entitled concentrated. From this concentrated solution, 5 mL was transferred to a 50 mL volumetric flask containing 9 mL fucose solution (200 mg/L) and diluted to 50 mL with deionized water. This sample was called diluted and had a fucose concentration of 40 mg/L. The diluted sample was then diluted 5 times more and used in the carbohydrate analysis.

The samples for the carbohydrate analysis are filtered through a 0.45 µm syringe filter into HPLC-vials. The vials are then ready for analysis, in this case a Dionex ISC5000 HPLC-system, equipped with CarboPac PA1 columns and an Electrochemical Detector.

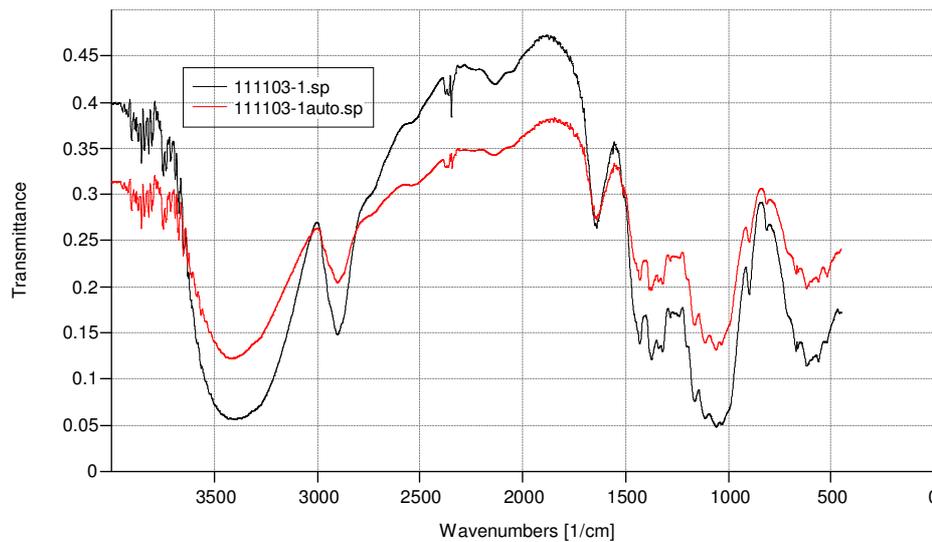
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<sup>7</sup> GC - Gas Chromatography, HPLC - High Performance Liquid Chromatography, CE - Capillary Electrophoresis

## 4. RESULTS AND DISCUSSION

### 4.1 IR-spectroscopy analysis

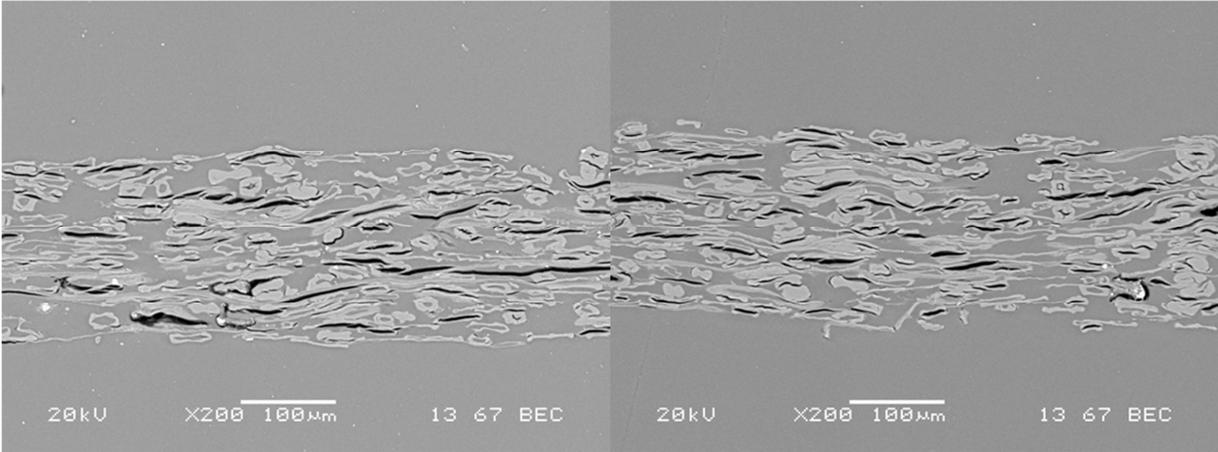
According to the literature, the crosslinking is suggested to occur from an ether bond between cellulose chains via hemiacetals formed from aldehydes produced during the retorting (Back, 1967). Formation of aldehydes should result in a carbonyl peak around  $1740\text{-}1690\text{ cm}^{-1}$  in an IR-spectrum and thereby indicate a structural change.



*Figure 4-1 IR-spectrum of non-retorted (1) and retorted (1auto) sheets.*

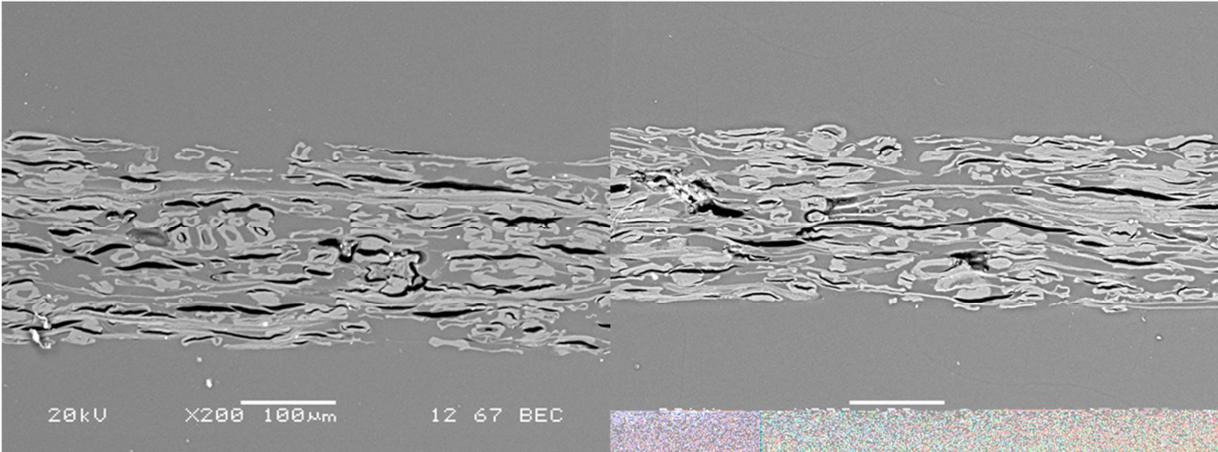
Both non-retorted and retorted samples were analysed using IR-spectroscopy and a comparison, shown in Figure 4-1, showed no difference. A possible reason could be the eventual changes being too small to be detected. The structural changes of the material can thereby not be proved to evaluate the increased wet strength effect in the material.

**4.2 SEM-pictures of non-retorted and retorted material**



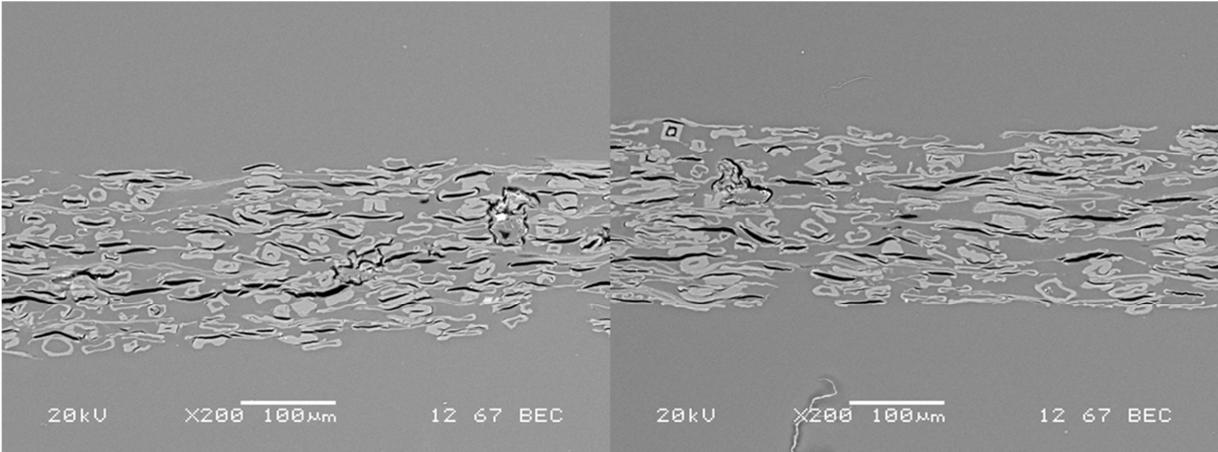
*Figure 4-2 Non-retorted reference.*

*Figure 4-3 Retorted reference.*



*Figure 4-4 Non-retorted xylan.*

*Figure 4-5 Retorted xylan.*



*Figure 4-6 Non-retorted HPC.*

*Figure 4-7 Retorted HPC.*

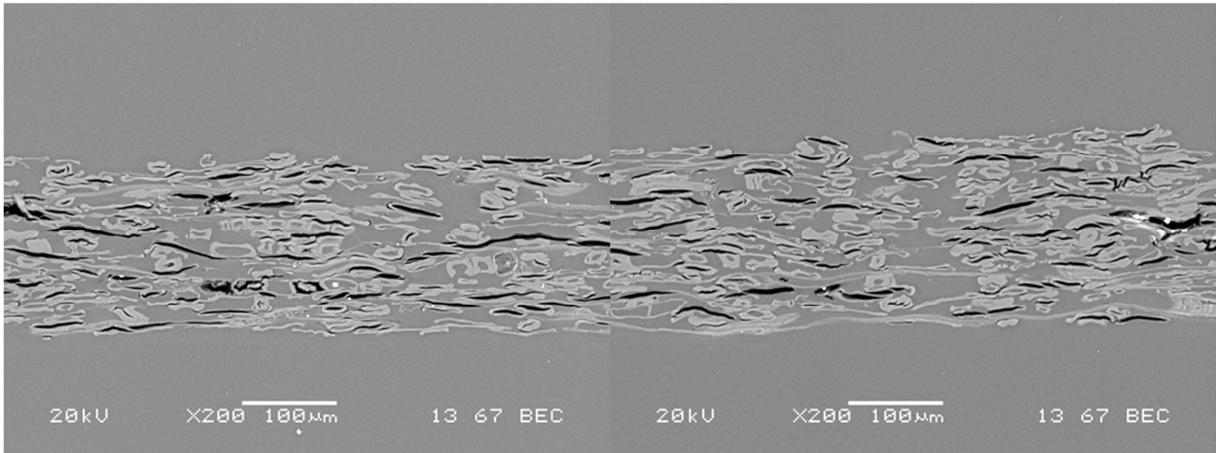


Figure 4-8 Non-retorted HPMC.

Figure 4-9 Retorted HPMC.

The SEM picture showed no obvious difference between the non-retorted and retorted material, for both materials with and without addition of different chemicals.

### 4.3 Temperature as an effect of disintegration

Previous research at Tetra Recart has shown that the same wet strength is not reached for a packaging pasteurized at 96°C as for a packaging retorted at 125°C. Therefore a temperature study was performed with an untreated packaging and with packaging treated at 96, 110 and 130°C.

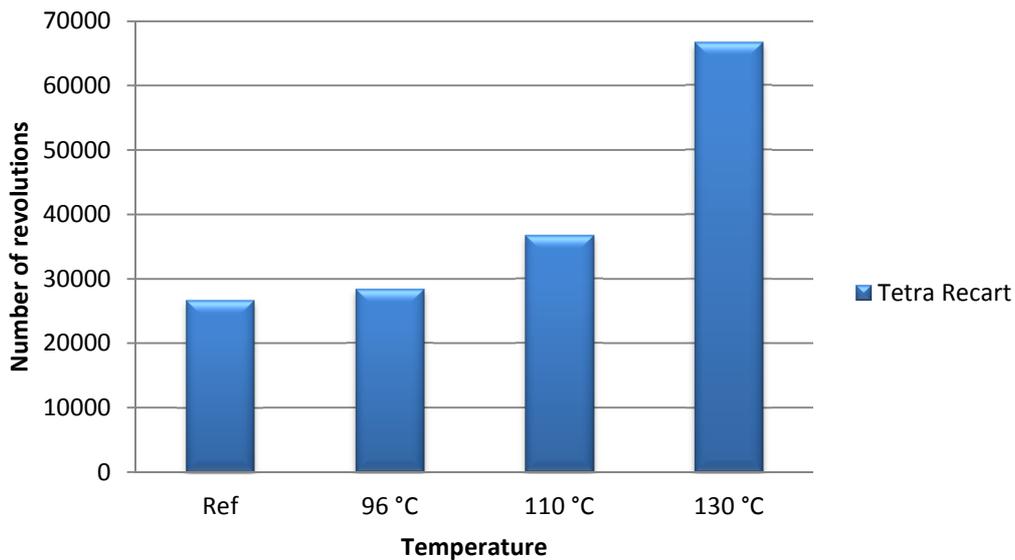


Figure 4-10 Graph of disintegration revolution for the actual product Tetra Recart heat-treated at different temperatures.

The study showed that the wet strength occur to some extent between 96 and 110°C but at the most between 110 and 130°C. This indicates that the activation energy for the wet strength reaction to occur probably is between 110 and 130°C, shown in Figure 4-10. Since some bacteria in specific food products survive below specific temperatures there is no option to decrease the retorting temperature below 110°C even though it might be a solution to the disintegration problem.

### 4.4 Addition of starch with and without AKD as an effect of disintegration

To evaluate the disintegration effect when different chemicals are added to unbleached SW and HW sheets, a study was made with variation of starch addition both with and without addition of AKD.

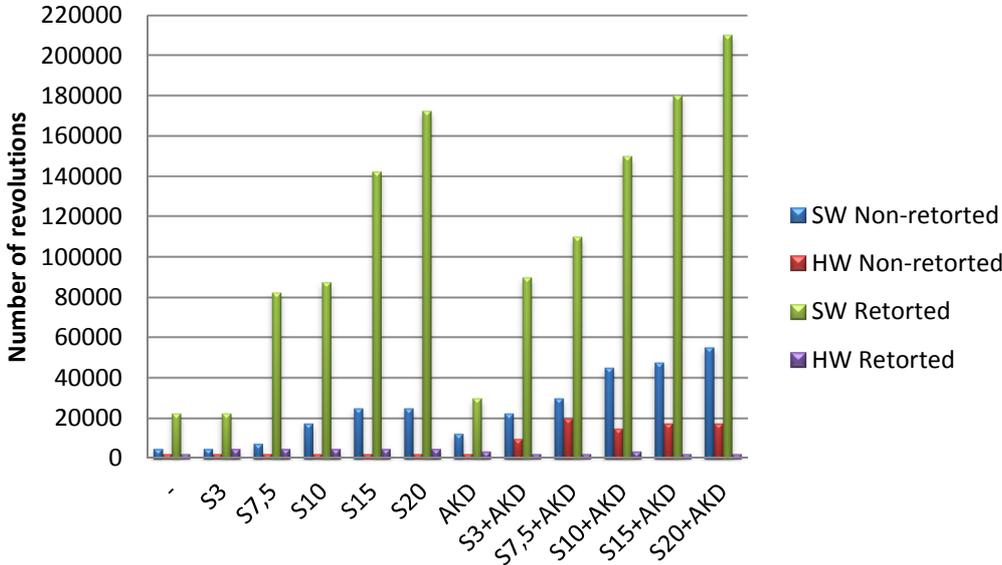


Figure 4-11 Graph of disintegration revolutions for starch sheets with and without AKD.

The results from study, shown in Figure 4-11, showed that no significant effect of starch addition could be seen for HW sheets both non-retorted and retorted.

A small effect could be seen for non-retorted SW sheets at 10 kg/ton and further up to 20 kg/ton. A major effect could be seen for retorted SW sheets at 7.5 kg/ton and the effect strongly increased with the amount of added starch. This effect could be explained by the starch ability to crosslink, when exposed to heat, with the remaining lignin in the pulp, which other studies have proved (Johansson et al., 2012).

When adding AKD to the sheets without any addition of starch the SW sheets, both non-retorted and retorted, increased in disintegration revolutions. As been previously mentioned, AKD increases the hydrophobicity of the fibres and keeps water from penetrating into the

fibres. It also has been proved that AKD can be used as a cross linker between fibres, which could be another explanation (Aulin et al., 2012). When curing AKD, the hydrophobic molecules will attach to the fibres and protect the structure over a longer time when being exposed to water (Fellers and Norman, 1996). The retorting is believed to act as an elongation of the curing and the AKD will bind even harder to the fibres and protect the structure even more after retorting. This applies only for SW sheets, which probably is due to HW fibres less ability of creating crossed and locked networks i.e. decreased possibility of bonding between fibres.

When adding starch together with AKD to SW sheets a much larger effect on the disintegration could be seen already at 3 kg/ton for both non-retorted and retorted. The disintegration revolutions increased throughout the whole study of starch together with AKD for SW sheets. The effect was though much larger for retorted SW sheets and an explanation for this could be the AKD-molecules anchoring the starch molecules to the surface of the fibre when being cured during retorting. The starch being a very large molecule could therefore be working as a cross linker between several fibres, generating a very large and water resistant network together with the anchoring by AKD. The small curing of the AKD in the production of the laboratory sheets is seen to be enough to create a visible effect also for the non-retorted sheets. There are though many other factors that could influence this behaviour which needs to be further investigated.

An interesting result, when adding both starch and AKD, is that non-retorted HW increased in disintegration revolutions a bit for all amounts of added starch but decreased again when retorted. This is probably due to decomposition, during retorting, of gained bonds between pulp material, starch and AKD and also confirms the theory of lack of network formation. The decomposition effect could be observed throughout the whole study of starch together with AKD.

An important point of view, when looking at these results, is the lignin content in the SW and HW pulp. Looking at the same conditions for several pulps with variable lignin contents would provide useful information about the different compounds included in the material.

## **4.5 Disintegration of laboratory sheets containing different chemicals**

The increased wet strength of liquid packaging board is claimed to occur through a crosslinking between cellulose chains. Therefore, a so-called spacer was added to both unbleached SW and HW pulp to increase the distance between the chains and thereby aggravate the crosslinking. The hemicellulose xylan, from beech, and three different cellulose derivatives was used in the sheets, later treated in the retorter. The last derivative, hydroxypropyl methylcellulose phthalate (HPMC-P), is a more hydrophobic derivative since it has a phthalate group and evaluated in this case for avoiding uptake of moisture during retorting, which influence the performance of the packaging. Figure 4-12 shows the number

of revolutions during disintegration for softwood and hardwood sheets with and without addition of chemical, both non-retorted and retorted.

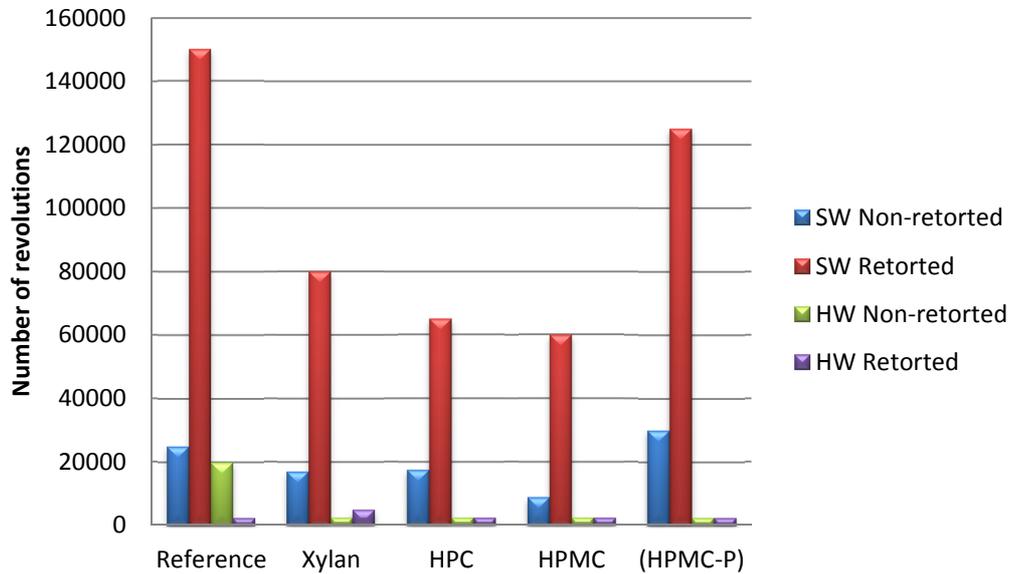


Figure 4-12 Graph of disintegration revolutions for sheets with and without addition of different chemicals.

The HW sheets were not affected by the addition of either xylan or a cellulose derivative. As for the starch with and without AKD study, the HW reference sheets showed decomposition when being retorted.

Addition of a cellulose derivative to SW sheets gave an effect in all cases, both for non-retorted and retorted sheets, except for HPMC-P, which is shown in Figure 4-12. The reason for this is probably due to the hydrophobic part in HPMC-P, interacting with AKD, enhancing the protection against water penetration. The parentheses around HPMC-P in the graph implies that the retorted sample was not able to disintegrate complete, fibres were stuck in the hydrophobic particles left in the sheet, and therefore a correct disintegration revolution could not be measured.

The derivative HPMC gave the most significant decrease in disintegration revolutions compared to the reference, for both non-retorted and retorted. An explanation for this could be the derivative adsorbing, just as xylan (Köhnke and Gatenholm, 2007), to the hydroxy groups on the fibre surfaces blocking the later added starch molecules from adsorbing on the surface and thereby preventing a strong network formation together with AKD. The same effect is seen for xylan and HPC, which is consistent with the theory of blocking hydroxy groups from starch adsorption.

Depending on how low the disintegration revolutions are wanted to be, both xylan and cellulose derivatives could be used to decrease the revolutions. An addition of xylan or a

cellulose derivative could be a solution for the difficult disintegration except an observation of all materials being very hydrophilic when exposed to water, which could be a problem for the packaging performance.

### 4.6 Lignin as an effect of disintegration

Previous studies at Korsnäs have indicated an increased wet strength with increased lignin content. To prove this, fully bleached sheets, without any chemical additions, were produced and retorted to compare with the unbleached sheets. To evaluate if difference in hemicellulose composition could take part of the increased wet strength both hardwood and softwood pulp were used.

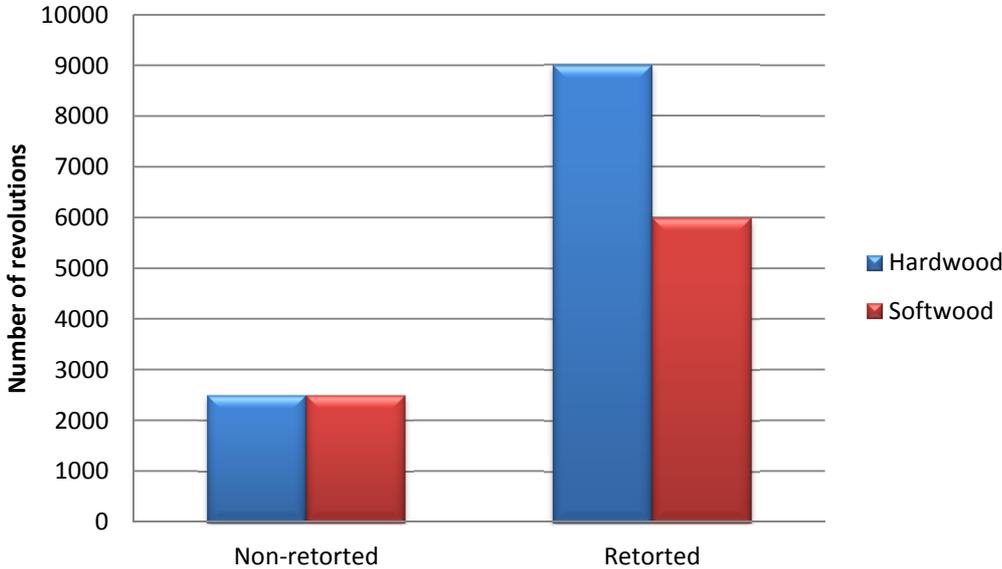


Figure 4-13 Graph of disintegration revolutions for fully bleached sheets.

Results showed that no large difference, between non-retorted and retorted sheets, could be seen and thereby the lignin is proved to have an influence on the wet strength development of the material during retorting. There were no large differences between hardwood and softwood pulp either and the hemicellulose composition is thereby believed to not be of importance for the phenomenon when having no chemical additions. To prove this, complementary analysis has to be performed.

As seen on the scale in Figure 4-13 for the disintegration revolutions, sheets made of bleached pulp is much easier to disintegrate why the difference looks much larger than they are, compared to differences when disintegrating sheets made of unbleached pulp.

## 4.7 Disintegration of laboratory sheets with addition of lignin or modified lignin

Based on the study of lignin as an effect of disintegration and literature suggesting formation of radicals from lignin during retorting (Felby et al., 2004), a purchased reference lignin and a modified lignin, described in the previous chapter, were added to fully bleached pulp. Lignin has been shown to adsorb on fibres in the same way as xylan does (Maximova et al., 2001) why it could be possible to evaluate the effect of lignin composition on disintegration. For comparison, reference sheets with starch and AKD were also made.

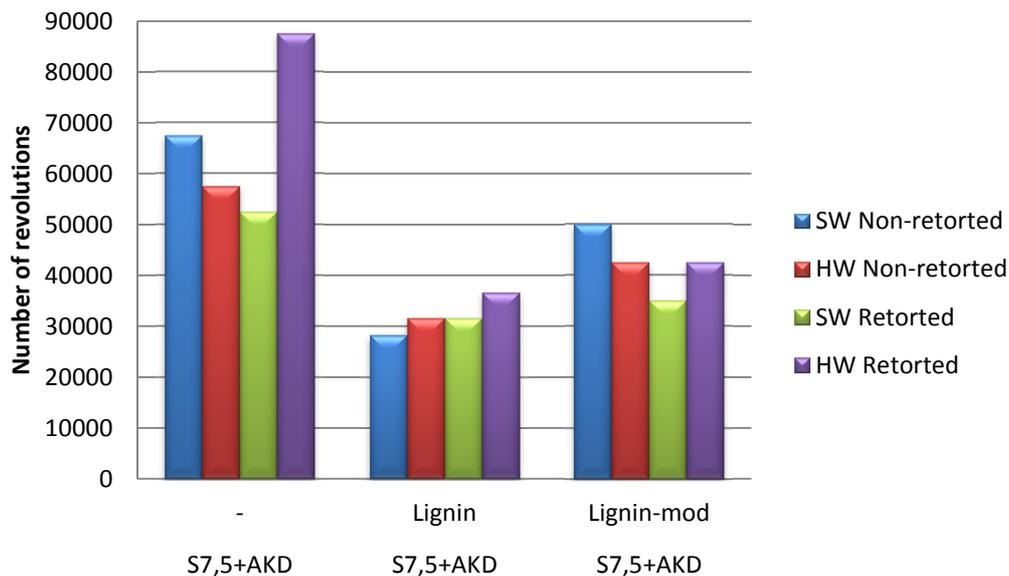


Figure 4-14 Graph of disintegration revolutions for sheets with addition of lignin or modified lignin.

The hypothesis of the lignin being the true reason for the increased wet strength during retorting could not be confirmed through this study. Mainly since the adsorbed lignin is not bound in the fibre in the same way as for unbleached pulp. It is also difficult to control how much of the lignin being adsorbed on the fibre surface, mostly since the modified lignin did not dissolve completely in the pulp mixture, but there were two other interesting results observed in the study.

The first interesting result from the study, shown in Figure 4-14, is the increased disintegration revolutions for retorted HW sheets, which has been the opposite for unbleached HW sheets. The reason for this could be the more exposed fibre surfaces when the lignin has been removed. HW fibres being much smaller than SW fibres and lignin being such a large molecule, the starch and AKD might now have a larger surface area to adhere to and create more dense hydrophobic interactions. This will give a larger effect on the disintegration of HW since it is on a smaller scale compared to SW.

SW on the other hand occurred to behave in the opposite way when being fully bleached compared to being unbleached. A result that needs to be further investigated in terms of for example amount of fibrils available for reaction and chemical composition, i.e. differences in hemicelluloses, in the fibres with for example SEM and carbohydrate analysis.

The second interesting result from the study showed that both lignin and modified lignin most likely adsorbs to the fibre surface, just as xylan, and blocks the starch to adsorb on the surface. The higher disintegration revolutions for the modified lignin are probably due to the modified lignin's more hydrophobic properties compared to the reference lignin.

#### 4.8 Disintegration of laboratory sheets with addition of an antioxidant

As mentioned before, literature indicates a formation of radicals from lignin during retorting (Felby et al., 2004). In order to investigate if the alleged radical formation could be hindered, an antioxidant was added to unbleached SW sheets.

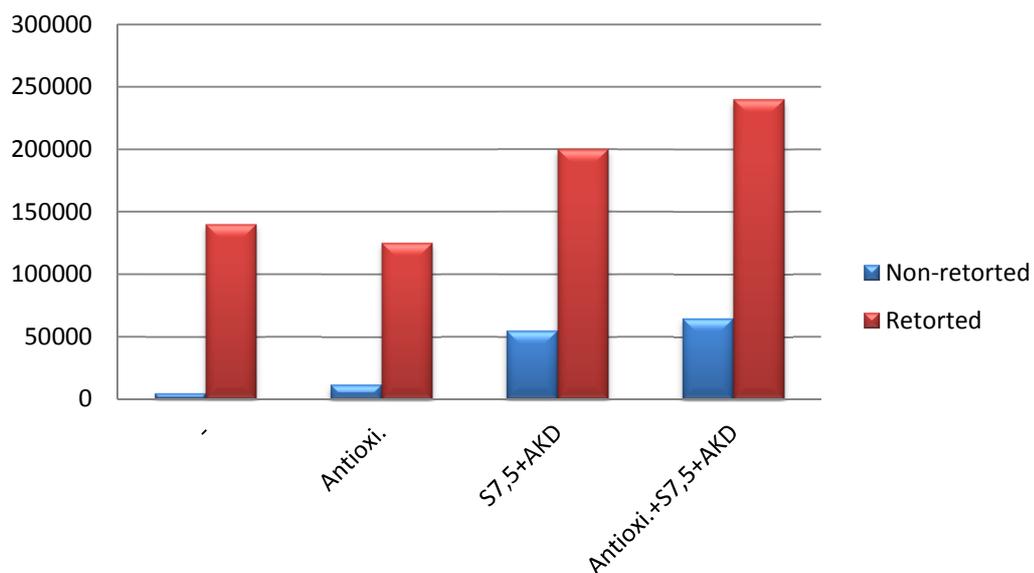


Figure 4-15 Graph of disintegration revolutions for SW sheets with addition of an antioxidant.

The results, shown in Figure 4-15, give no signs of the antioxidant hindering the increased wet strength during retorting rather than enhancing it. A possible explanation for this could be the hydrophobicity of the antioxidant, not completely dissolving in the pulp mixture when added. To get a more direct answer on its effect on disintegration a more water soluble antioxidant would be suitable.

## 4.9 Retorting in N<sub>2</sub>-atmosphere

The formation of lignin radicals formed during retorting is said to be initiated by an oxidation with oxygen (Widsten and Kandelbauer, 2008). The retorting was therefore performed in nitrogen atmosphere instead of air.

*Table 4-1 Retorting in nitrogen atmosphere*

Retorting	Number of disintegration revolutions
Air	200 000
Nitrogen	195 000

The results, shown in Table 4-1, of disintegration revolutions for sheets retorted in nitrogen were though equal to the ones measured for sheets retorted in air. In order to evaluate the influence of oxygen more exactly, a retorting in totally inert atmosphere could be performed. It would also be interesting to use an organic solvent instead of water to avoid trapped oxygen in the water, able to oxidize the material.

## 4.10 Klason and acid soluble lignin content before and after retorting

According to the literature, lignin is degraded during heat-treatment forming lignin fragments and lignin radicals able to crosslink fibres together (Felby et al., 2004). A retorted sample should therefore have a decreased amount of Klason lignin, which is gravimetrically measured, since the large lignin molecule is decomposed and the small fragments bound in to the fibres.

*Table 4-2 Klason lignin content in reference pulp and retorted pulp.*

Sample	Weight (g)	Filter (g)	Dried sample (g)	Klason lignin (g)	%	Average %
Non-retorted	0.2147	0.1028	0.1189	0.0161	7.5	
Non-retorted	0.2082	0.1019	0.1167	0.0148	7.1	
Non-retorted	0.2310	0.1039	0.1220	0.0181	7.8	<b>7.5</b>
Retorted	0.2063	0.0982	0.1129	0.0147	7.1	
Retorted	0.2018	0.1037	0.1182	0.0145	7.2	
Retorted	0.2182	0.0987	0.1142	0.0155	7.1	<b>7.1</b>

Table 4-2 shows that retorted samples have a lower average percentage, 0.5%, of Klason lignin than non-retorted samples. The result is a repeating trend indicating a change in lignin composition during retorting.

*Table 4-3 Acid soluble lignin in reference pulp and retorted pulp.*

Sample	m (g)	Absorbance	ASL (%)	Average (%)
Non-retorted	0.2185	0.1862	0.85	
Non-retorted	0.2180	0.1973	0.91	<b>0.88</b>
Retorted	0.2142	0.1934	0.90	
Retorted	0.2137	0.2278	1.07	<b>0.98</b>

The hydrolysis performed to measure Klason lignin also generates acid soluble lignin (ASL), measured with an UV spectrometer at 205 nm. Table 4-3 shows that retorted samples have somewhat more acid soluble lignin than the reference samples, but the difference is very small.

In order to follow the indicated degradation and change in composition of lignin during retorting, a longer retorting of 1.5 and 2 hours was made.

*Table 4-4 Klason lignin after 1.5 h and 2 h retorting.*

Sample	Weight (g)	Filter (g)	Dried sample (g)	Klason lignin (g)	%	Average %
Retorted 1.5	0.2040	0.1036	0.1191	0.0155	7.6	
Retorted 1.5	0.2018	0.0995	0.1140	0.0145	7.2	
Retorted 1.5	0.2104	0.1043	0.1202	0.0159	7.6	<b>7.5</b>
Retorted 2	0.2031	0.1018	0.1171	0.0153	7.5	
Retorted 2	0.2033	0.1035	0.1191	0.0156	7.7	<b>7.7</b>

Table 4-4 shows that a longer retorting actually increases the amount of Klason lignin. An explanation for this could be a repolymerization of the formed lignin monomers and radicals when retorted for a longer time than 1 hour, which apparently initiates a depolymerisation of the lignin.

## 4.11 Carbohydrate analysis of non-retorted and retorted sheets

The sugar monomer containing hydrolysate, generated during the acid hydrolysis, could indicate eventual differences between non-retorted and retorted pulp in a carbohydrate analysis.

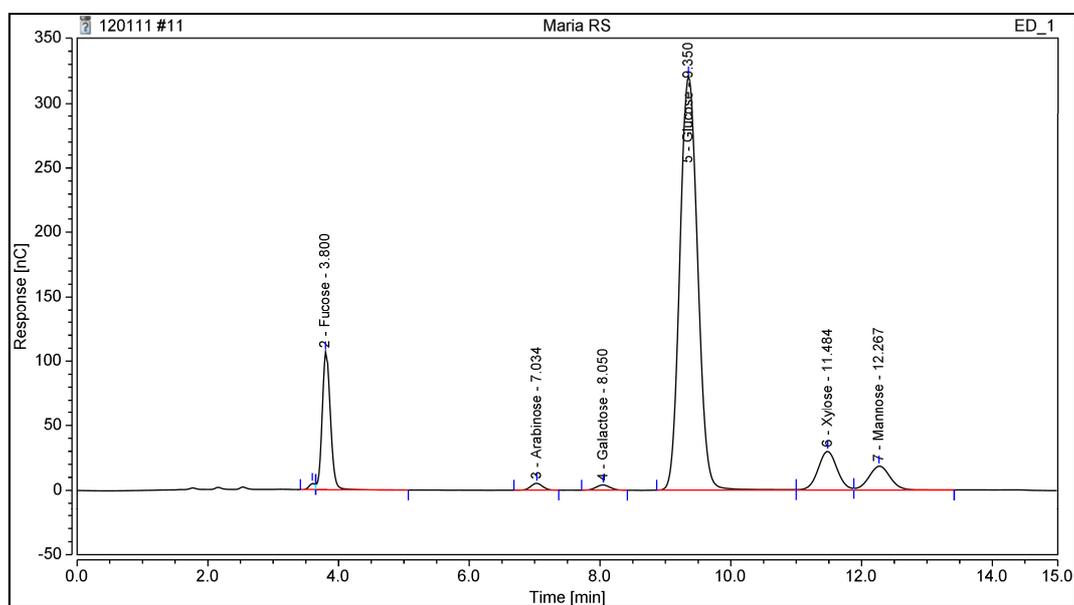


Figure 4-16 Carbohydrate analysis of non-retorted pulp.

Table 4-5 Carbohydrate analysis of non-retorted pulp.

Integration Results							
No.	Peak Name	Retention Time <i>min</i>	Area <i>nC*min</i>	Height <i>nC</i>	Relative Area <i>%</i>	Relative Height <i>%</i>	Amount <i>mg/L</i>
2	Fucose	3.800	15.688	106.576	11.50	21.78	n.a.
3	Arabinose	7.034	1.114	5.323	0.82	1.09	0.5162
n.a.	Rhamnose	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4	Galactose	8.050	1.015	4.066	0.74	0.83	0.3662
5	Glucose	9.350	101.156	320.437	74.13	65.49	40.4863
6	Xylose	11.484	10.023	29.778	7.34	6.09	3.9480
7	Mannose	12.267	6.972	18.367	5.11	3.75	3.3708
<b>Total:</b>			<b>135.968</b>	<b>484.548</b>	<b>99.64</b>	<b>99.03</b>	<b>48.69</b>

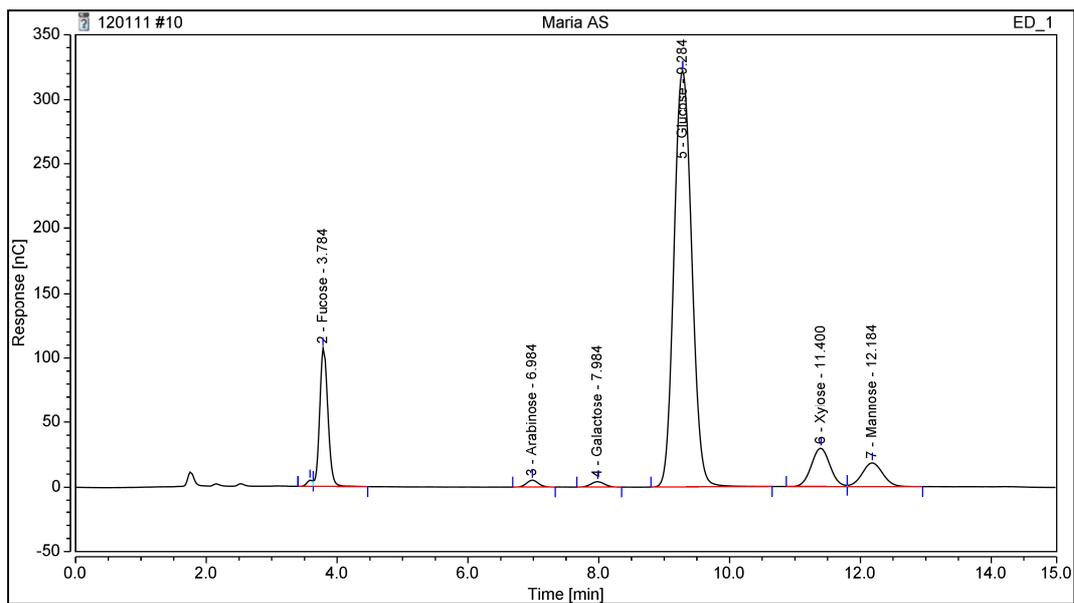


Figure 4-17 Carbohydrate analysis of retorted pulp.

Table 4-6 Carbohydrate analysis of retorted pulp.

Integration Results							
No.	Peak Name	Retention Time <i>min</i>	Area <i>nC*min</i>	Height <i>nC</i>	Relative Area <i>%</i>	Relative Height <i>%</i>	Amount <i>mg/L</i>
2	Fucose	3.784	15.649	107.231	11.53	21.84	n.a.
3	Arabinose	6.984	1.113	5.327	0.82	1.08	0.5171
n.a.	Rhamnose	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4	Galactose	7.984	1.023	4.188	0.75	0.85	0.3701
5	Glucose	9.284	101.038	321.800	74.44	65.55	40.5575
6	Xylose	11.400	9.736	29.450	7.17	6.00	3.8425
7	Mannose	12.184	6.682	18.169	4.92	3.70	3.2422
<b>Total:</b>			<b>135.241</b>	<b>486.165</b>	<b>99.64</b>	<b>99.03</b>	<b>48.53</b>

The carbohydrate analysis for non-retorted and retorted SW pulp showed no significant differences. Why the answer to the increased wet strength before and after retorting of the reference board cannot be explained, in this case, by the chemical composition of the pulp shown in Table 4-5 and Table 4-6.

## 5. CONCLUSIONS AND FUTURE OUTLOOK

In this thesis a general mapping has been performed, through several analyses, of how the properties of the involved compounds in the liquid packaging board influences the increased wet strength.

IR-spectroscopy of the material showed that no differences could be seen for non-retorted and retorted sheets. The reason for this is probably due to too small differences in the material which are not detectable by IR-spectroscopy. A carbohydrate analysis of the non-retorted and the retorted material did not either show any obvious differences in chemical composition. Interesting chemical analysis to use in the future could be NMR or MS<sup>8</sup> in order to search for a molecular difference between the non-retorted and the retorted material.

A temperature study was performed in order to encircle the interval where the actual wet strength increase occurs. The study showed that retorting between 110°C and 130°C, makes the material more difficult to disintegrate.

The materials sizing agent AKD and retention aid cationic starch were evaluated to investigate their influence on disintegration before and after retorting. The study showed that starch alone has a large effect on disintegration for softwood pulp after retorting but only a slight effect on disintegration of hardwood pulp after retorting. A result with a possible explanation of softwood having the ability to form more internal bonding through crossed and locked fibres and the fact that starch can crosslink to lignin when exposed to heat. Softwood containing more lignin than hardwood makes it more susceptible to the crosslinking with starch.

Starch in combination with AKD increases the disintegration revolutions even further for softwood pulp both before and after retorting. An anchoring of the starch molecules by AKD-molecules, creating a large network of the long and crosslinking starch molecules and the crossed fibres, could be a possible explanation for this. The same effect could not be seen for hardwood pulp, probably due to the short fibres less ability of network formation and creation of a locked structure.

The addition of the hemicellulose xylan or different cellulose derivatives, with the function of a blocker or a spacer in the sheets, was shown to give sufficient decrease in disintegration revolutions for both non-retorted and retorted sheets. Based on the results from the starch study an explanation for this could be the xylan or cellulose derivative blocking the hydroxy groups on the fibres and preventing adsorption of starch to the fibres. Thereby, the formation of a larger network of crossed fibres and crosslinking starch molecules were hindered. The addition of xylan or cellulose derivatives did hinder the increased wet strength phenomenon but showed a bit too large hydrophilic behaviour, why a more hydrophobic cellulose derivative was investigated. The hydrophobic cellulose derivative was though seen and believed to interact with the other hydrophobic parts in the material, i.e. AKD and lignin, rather enhancing than reducing the difficult disintegration of the sheets.

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<sup>8</sup> MS – Mass spectroscopy

Lignin was shown to have an impact on disintegration and a hypothesis of lignin radical formation, creating a cross-linked network, during retorting was evaluated.

Adsorption of lignin and a modified lignin on fully bleached pulp was attempted to be used as a model for lignin's impact on disintegration. The result was not sufficient as evidence for lignin creating a cross-linked structure but it did confirm the theory of xylan or a cellulose derivative blocking hydroxyl groups on the fibres. Thus, preventing starch from adhering onto the fibres as the same effect was shown for the adsorption of lignin onto the fibres. Addition of an antioxidant as a hindrance of radical formation of lignin was not successful because of the antioxidant incapability of dissolving in the pulp mixture.

Klason lignin and acid soluble lignin was measured and results showed a decrease in Klason lignin for retorted pulp compared to non-retorted pulp. These results indicate a depolymerisation of the lignin, possibly decomposing in to lignin radicals. When retorting the material a longer time than standard the Klason lignin was shown to increase again. A reasonable explanation for this could be a repolymerization of the lignin monomers, creating an even larger cross-linked network than before and thereby further enhance the difficult disintegration.

Retorting in nitrogen atmosphere was tried but did not provide any decrease in disintegration revolutions for the material. The problem in this case was probably the non-closed system. Oxygen as the oxidizing substrate could be more thorough investigated by retorting the material in a proved completely inert atmosphere and by the use an organic solvent, instead of water, to avoid any trapped oxygen in process.

Interesting future work would be to prove the hindrance of starch adsorbing onto the fibres when adding xylan, lignin or a cellulose derivative.

It would also be interesting to make a more thorough mapping of the differences between softwood and hardwood pulp as for bleached and unbleached pulp. For example by the use of carbohydrate analysis, SEM, NMR and MS to understand why the opposite effect of the disintegration occurs for some cases mentioned in the thesis.

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## APPENDIX

Disintegration revolutions for all experimental evaluations:

### *Temperature study*

Temperature	Disintegration 1	Disintegration 2	Disintegration 3	Average
Ref	25000	30000	25000	26667
96 °C	25000	30000	30000	28333
110 °C	40000	35000	35000	36667
130 °C	75000	60000	65000	66667

### *Addition of different chemicals – non-retorted*

Material	Add. 1	Add. 2	Add. 3	Disintegration 1	Disintegration 2	Disintegration 3	Average
Unbleached SW	S7.5	AKD	-	20000	25000	30000	25000
Unbleached SW	S7.5	AKD	xylan	15000	20000	15000	16667
Unbleached SW	S7.5	AKD	HPC	17500	17500	17500	17500
Unbleached SW	S7.5	AKD	HPMC	10000	7500	10000	9167
Unbleached SW	S7.5	AKD	HPMC-P	25000	35000	-	30000
Unbleached HW	S7.5	AKD	-	20000	20000	-	20000
Unbleached HW	S7.5	AKD	xylan	2500	2500	-	2500
Unbleached HW	S7.5	AKD	HPC	2500	2500	-	2500
Unbleached HW	S7.5	AKD	HPMC	2500	2500	-	2500
Unbleached HW	S7.5	AKD	HPMC-P	2500	2500	-	2500

*Addition of different chemicals – retorted*

<b>Material</b>	<b>Add. 1</b>	<b>Add. 2</b>	<b>Add. 3</b>	<b>Disintegration 1</b>	<b>Disintegration 2</b>	<b>Disintegration 3</b>	<b>Average</b>
Unbleached SW	S7.5	AKD	-	150000	150000	-	150000
Unbleached SW	S7.5	AKD	xylan	75000	75000	90000	80000
Unbleached SW	S7.5	AKD	HPC	80000	17500	17500	38333
Unbleached SW	S7.5	AKD	HPMC	45000	60000	75000	60000
Unbleached SW	S7.5	AKD	HPMC-P	125000	-	-	125000
Unbleached HW	S7.5	AKD	-	2500	2500	-	2500
Unbleached HW	S7.5	AKD	xylan	5000	5000	-	5000
Unbleached HW	S7.5	AKD	HPC	2500	2500	-	2500
Unbleached HW	S7.5	AKD	HPMC	2500	2500	-	2500
Unbleached HW	S7.5	AKD	HPMC-P	2500	2500	-	2500

*Variation of starch with and without AKD – non-retorted*

<b>Material</b>	<b>Add. 1</b>	<b>Add. 2</b>	<b>Add. 3</b>	<b>Disintegration 1</b>	<b>Disintegration 2</b>	<b>Average</b>
Unbleached SW	-	-	-	5000	5000	5000
Unbleached SW	S3	-	-	5000	5000	5000
Unbleached SW	S7,5	-	-	5000	10000	7500
Unbleached SW	S10	-	-	15000	20000	17500
Unbleached SW	S15	-	-	25000	25000	25000
Unbleached SW	S20	-	-	25000	25000	25000
Unbleached SW	-	AKD	-	10000	15000	12500
Unbleached SW	S3	AKD	-	20000	25000	22500
Unbleached SW	S7,5	AKD	-	30000	30000	30000
Unbleached SW	S10	AKD	-	45000	45000	45000
Unbleached SW	S15	AKD	-	45000	50000	47500
Unbleached SW	S20	AKD	-	55000	55000	55000
Unbleached HW	-	-	-	2500	2500	2500
Unbleached HW	S3	-	-	2500	2500	2500
Unbleached HW	S7,5	-	-	2500	2500	2500
Unbleached HW	S10	-	-	2500	2500	2500
Unbleached HW	S15	-	-	2500	2500	2500
Unbleached HW	S20	-	-	2500	2500	2500
Unbleached HW	-	AKD	-	2500	2500	2500
Unbleached HW	S3	AKD	-	7500	12500	10000
Unbleached HW	S7,5	AKD	-	20000	20000	20000
Unbleached HW	S10	AKD	-	15000	15000	15000
Unbleached HW	S15	AKD	-	20000	15000	17500
Unbleached HW	S20	AKD	-	10000	25000	17500

*Variation of starch with and without AKD – retorted*

<b>Material</b>	<b>Add. 1</b>	<b>Add. 2</b>	<b>Add. 3</b>	<b>Disintegration 1</b>	<b>Disintegration 2</b>	<b>Average</b>
Unbleached SW	-	-	-	25000	20000	22500
Unbleached SW	S3	-	-	20000	25000	22500
Unbleached SW	S7,5	-	-	95000	70000	82500
Unbleached SW	S10	-	-	105000	70000	87500
Unbleached SW	S15	-	-	130000	155000	142500
Unbleached SW	S20	-	-	155000	190000	172500
Unbleached SW	-	AKD	-	25000	35000	30000
Unbleached SW	S3	AKD	-	90000	-	90000
Unbleached SW	S7,5	AKD	-	110000	-	110000
Unbleached SW	S10	AKD	-	150000	-	150000
Unbleached SW	S15	AKD	-	180000	-	180000
Unbleached SW	S20	AKD	-	210000	-	210000
Unbleached HW	-	-	-	2500	2500	2500
Unbleached HW	S3	-	-	5000	5000	5000
Unbleached HW	S7,5	-	-	5000	5000	5000
Unbleached HW	S10	-	-	5000	5000	5000
Unbleached HW	S15	-	-	5000	5000	5000
Unbleached HW	S20	-	-	5000	5000	5000
Unbleached HW	-	AKD	-	5000	2500	3750
Unbleached HW	S3	AKD	-	2500	2500	2500
Unbleached HW	S7,5	AKD	-	2500	2500	2500
Unbleached HW	S10	AKD	-	2500	5000	3750
Unbleached HW	S15	AKD	-	2500	2500	2500
Unbleached HW	S20	AKD	-	2500	2500	2500

*Addition of lignin and modified lignin – non-retorted*

<b>Material</b>	<b>Add. 1</b>	<b>Add. 2</b>	<b>Add. 3</b>	<b>Disintegration 1</b>	<b>Disintegration 2</b>	<b>Disintegration 3</b>	<b>Average</b>
Bleached SW	-	-	Lignin-mod	2500	2500	-	2500
Bleached SW	S7,5	AKD	-	70000	65000	-	67500
Bleached SW	S7,5	AKD	Lignin	25000	35000	25000	28333
Bleached SW	S7,5	AKD	Lignin-mod	50000	50000	-	50000
Bleached HW	-	-	Lignin-mod	2500	2500	-	2500
Bleached HW	S7,5	AKD	-	55000	60000	-	57500
Bleached HW	S7,5	AKD	Lignin	30000	35000	30000	31667
Bleached HW	S7,5	AKD	Lignin-mod	35000	50000	-	42500

*Addition of lignin and modified lignin – retorted*

Material	Add. 1	Add. 2	Add. 3	Disintegration 1	Disintegration 2	Disintegration 3	Average
Bleached SW	-	-	Lignin-mod	10000	10000	-	10000
Bleached SW	S7,5	AKD	-	55000	50000	-	52500
Bleached SW	S7,5	AKD	Lignin	40000	25000	30000	31667
Bleached SW	S7,5	AKD	Lignin-mod	35000	35000	-	35000
Bleached HW	-	-	Lignin-mod	10000	10000	-	10000
Bleached HW	S7,5	AKD	-	85000	90000	-	87500
Bleached HW	S7,5	AKD	Lignin	40000	35000	35000	36667
Bleached HW	S7,5	AKD	Lignin-mod	50000	35000	-	42500

*Addition of an antioxidant – non-retorted*

Material	Add. 1	Add. 2	Add. 3	Disintegration 1	Disintegration 2	Disintegration 3	Average
Bleached SW	S7,5	AKD	Anti.	60000	70000	65000	65000
Bleached SW	S7,5	-	Anti.	15000	10000	10000	12500

*Addition of an antioxidant – retorted*

Material	Add. 1	Add. 2	Add. 3	Disintegration 1	Disintegration 2	Disintegration 3	Average
Bleached SW	S7,5	AKD	Anti.	240000	-	-	240000
Bleached SW	S7,5	-	Anti.	140000	-	-	140000