Optimisation of bleaching of non-wood cellulose for cosmetics and food applications

Turning oat husks from waste to product

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Master's thesis

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Cellulose itself is white, but in natural materials, it is tightly bound to lignin and hemicellulose. The purpose of bleaching is to break down and remove the lignin that gives colour to the cellulose, allowing cellulose to show its natural whiteness. The dark colour of lignin is due to its multiple aromatic structures and the conjugated double bonds.

Over the years, cellulose bleaching has undergone significant advancements and evolution cycles in the paper industry. The goal is to remove lignin as efficiently as possible while maintaining the fibre properties of cellulose enough for the intended end products to be manufactured. The evolution of bleaching was often induced by cost and efficiency targets but lately also from environmental concerns.

Cellulose is used as a filler in the food industry, where it helps modify the texture of food. However, since cellulose is not broken down in the human body, its nutritional value is negligible and as dietary fibre it helps the digestion system with many positive health effects. For food industry applications, a brown, strongly colouring cellulose is generally undesirable.

Firstly, in cosmetic products, cellulose is used among other purposes as a filler to provide a thick consistency. Secondly, In September 2023, EU banned the use of plastic microbeads in commercial products. Small plastic beads were used in exfoliating face creams, but cellulose-based microparticles could serve as an alternative in this market. As in food applications, in cosmetic applications it is important that the cellulose blend seamlessly into traditionally white creams.

This study investigates the optimal bleaching process for non-wood oat husk cellulose produced at CH-Bioforce's pilot plant. Two chemicals, hypochlorite and hydrogen peroxide, are used with various reaction conditions to optimise bleaching reaction chain while maintaining adequate fibre properties. With many conditions to optimise, design of experiment software is used to lesser the number of tests. While cellulose bleaching is well-studied in the paper industry, wood as a raw material differs significantly in terms of bleaching requirements. Due to non-woods' lower content of colour-inducing lignin, a milder bleaching approach can be applied.

Experiment is done with the help of a design of experiments software to try to find the optimal bleaching approach. Small batch bleaching reactions are done with chemicals called sodium hypochlorite and hydrogen peroxide. Pulp brightness and degree of polymerisation is then measured to analyse whiteness and the length of cellulose strands. Additionally, some measurements of alpha cellulose and kappa number are made to know what happens during bleaching.

Keywords: agricultural waste stream, bleaching, cellulose, circular economy, elemental chlorine free, non-wood, oat husk

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1 Introduction

Large volumes of agricultural biowaste are generated globally each year, much of which is commonly incinerated for energy recovery. While this practice provides a convenient method of disposal and contributes to heat and power generation, it also leads to the release of greenhouse gases and the loss of valuable biomass resources. In the context of climate change mitigation and the transition towards a circular economy, there is growing interest to steer such waste from incineration and instead developing it into high-value products. Non-wood lignocellulosic residues, such as wheat straw, sugarcane bagasse and other crop by-products, represent a renewable and underutilized source of cellulose. Rather than being treated as waste, these materials could be processed to be used as cellulose products suitable in food, pharmaceuticals and cosmetics.

With the lessening supply of wood raw material, the growing importance of nature preservation and the usefulness of forests as carbon sinks, wood use for pulping and especially for energy can be seen as wasteful. Particularly, when alternative raw materials for pulping are known and already used for millions of tonnes of cellulose pulp. (Sapuan, Ainun, Zakiah, et al. 2023)

Finnish agriculture produces oats, and their husks are gathered with the grain and only removed from the grain at the mill. That is an example of a point source waste which could be easily utilised. To achieve value from the waste materials, they could be more valuable when fractionated. It allows different components of the waste material to be separated and then sold. CH-Bioforce has achieved this with oat husks and the separation of hemicellulose, lignin and cellulose from them. It can be done lessening waste and reusing the material to become new useful product again. Fractionation technologies can be used with almost any kind of biomass as they all contain same products but of course in different amounts. CH-Bioforce's raw material is oat husks (or hulls) which are the cover of the grain in oat and other cereals. Oat husks are an easy the utilise raw material as it is a point source waste. When grain is harvested, husks are on the grain and separated only in the milling process at the oat mill where the husk can be gathered from as a point source. The competing process for this material is its burning value.

Many waste materials are difficult to incorporate into an already existing system, such as the wood pulping system. The pulp and paper industry needs huge amounts of wood as its raw material, and it is difficult to switch. There are many changes to consider and alter if switching to a non-wood source for cellulose is interesting.

Firstly, the availability or location of agricultural waste as it is all around the vast fields across countrysides. Transportation of the raw material represents a significant share of the production-costs, considering that the raw material is otherwise cheap. Many waste streams need to be sourced from various farms and are seasonal. They are not easy to handle and would need specific machinery to pack effectively (Bajpai 2018). If gathering for example the stalks is not common practise as is the case with cereal grains, gathering the stalks becomes an additional costly step which raises the price. Secondly an adjacent challenge is the storage and handling of the raw materials (Sapuan, Ainun, and Ilyas 2023). At least in the north all crops are seasonal products, thus the waste gathering time is short and storage time is long, which adds need for storage space. Storage needs to be more elaborate as non-wood products are more susceptible to deterioration by wetness and microorganisms than wood is. This raw material would probably need a packaging like hay and other animal feed (Sapuan, Ainun, Zakiah, et al. 2023). Deterioration from storage leads to difficulties in bleaching as pulp might not respond to the bleaching as expected. If deterioration happens it would make the non-woods from comparatively easier to bleach to possibly becoming more difficult to bleach with the need of pretreatments like enzymatic reactions (Abd El-Sayed et al. 2020). In chemical recovery from effluents and therefore environmentally, non-wood reactions can be worse, but the reasons are largely caused by the economy of scale. Larger mills have more responsibility to manage their waste but can also invest more capital to better chemical recovery systems (Sapuan, Ainun, Zakiah, et al. 2023). Also, silica which is present more in non-wood species affects black liquor which is a waste material to be very viscous. Silica also causes scaling in the production machinery which need more cleaning. (Yuan et al. 2016) Lastly, agricultural waste materials are diverse and more difficult to utilise than wood as they have uneven chemical properties between species and growing conditions. Wood is more similar all around the year and with different growing conditions. Wood has also been studied and used for already decades. (Sapuan, Ainun, and Ilyas 2023)

Oat husks and other non-wood materials are advantageous as raw materials for the lower lignin amounts with values starting as low as 2-4 percent from hemp to around 20-30 percent of bamboo. Wood materials have a lignin percent of 27-32 % which is at the top of bamboo materials. Lower lignin amounts account for less requirement for bleaching. Non-wood raw materials are lighter in colour than wood materials and bleaching chemical use is lower with them. Non-wood materials and oat husks are cheap as a raw material, usually only used for incineration. Non-wood plants yearly cultivation times are faster and easier to manage as wood growing is a done for decades. The varied raw materials also can be used to their advantages more than wood materials. (Sapuan, Ainun, and Ilyas 2023)

1.1 Cellulose, hemicellulose and lignin

Cellulose and hemicellulose are two of the primary structural components of plant biomass, forming the plant primary cell wall. These biopolymers contribute mechanical strength, flexibility and resiliency to plant tissues. Lignin is added when plants produce secondary cell walls which are stiffer, water resistant and less permeable. While cellulose is found mostly in terrestrial plants, it can also be produced by some algae as well, reflecting its widespread occurrence across nature. Cellulose being all around the natural landscape makes it the most abundant bio-compound in the world (Ek 2009). In cell walls cellulose organizes into microfibrils that create a network of strong yet flexible fibres, playing a crucial role in maintaining plant strength, shape, and structural integrity. Hemicellulose fills the cellulose microfibril gaps and connects them together by making hydrogen bonds between microfibrils. Then in secondary cell walls lignin is polymerised around the cellulose and hemicellulose to fill more of the gaps with lignin polymer. Lignin makes hydrogen bonds to both hemicellulose and cellulose fibres. Secondary cell walls become like a natural micro-composite material where lignin is the stiff binder and celluloses are the solid stretch resistant fibre. In non-wood plants cellulose fibre length can vary significantly from 0,6 mm long to 26 mm long (Azeez 2018).

1.1.1 Cellulose

Cellulose is a polysaccharide, a polymer consisting of many sugars connected, in this case β-glucoses, with a general formula of $(C_6H_{10}O_5)_n$. Glucoses are linked together rotating 180 ° and thus cellulose chains are structurally linear. Linking is from the first carbon to next saccharide’s fourth carbon. Cellulose chains in pulping have 300 to 1700 individual saccharides in chains and that is called the degree of polymerisation (DP). In nature, cellulose can be even longer as for example in cotton where cellulose chains can reach DP of 10 000 and above. (Tekin et al. 2014)

Each cellulose glucose monomer has three hydroxyl groups which allow cellulose to make several hydrogen bonds. Hydrogen bonds are made within the cellulose molecule as well as to other molecules. Hydrogen bonding abilities influence the limited solubility to most solvents, the reactivity of hydroxyl groups and the crystallinity of cellulose samples. Hydrogen bonds happen within the cellulose chain intramolecularly and to other cellulose molecules intermolecularly. Hydrogen bonds to other molecules allow the formation of cellulose microfibrils where multiple single cellulose molecule strands bind together to make larger fibre which is stronger but flexible at the same time. Cellulose hydrogen bonds allow multiple cellulose strands to attach themselves together in various three-dimensional arrangements. Different arrangements of cellulose strands affect the microfibril properties like stiffness or rigidity. These three-dimensional arrangements help cellulose to crystallise and to form fibrillar structures. (Rojas 2016)

There are two main types of natural cellulose which differ in the amount of hydrogen bonding intra-, and intermolecularly. Cellulose I, which has more intramolecular hydrogen bonds as glucose's hydroxyl groups from carbon two and three make hydrogen bonds to the previous and next glucose molecules with hydroxyl group from carbon six makes one bond intramolecularly and a second one intermolecularly. To summarise, three bonds to itself and one to outside molecules. Cellulose II has one more hydrogen bond available to other molecules but has also intramolecular bonds at carbon three hydroxyl group to next glucose's oxygen. In cellulose II the hydroxyl groups from carbon two and six are spread out of the glucose backbone and searching for hydrogen bonds to other molecules with a ratio of one intramolecular to two intermolecular hydrogen bonds. Two cellulose systems lead to different types of three-dimensional arrangements where the cellulose II is more densely packed and less reactive than cellulose I. Cellulose I hydrogen bonds are located along a plane which makes cellulose I assemble in layers. (Rojas 2016)

1.1.2 Hemicellulose

Hemicelluloses as a group is the second most abundant biopolymer in all plant mass with approximately 20-30 % of dry weight of most wood species (Tekin et al. 2014). But non-wood species usually have higher percentages of hemicellulose as the amount of lignin is smaller than in woods (Azeez 2018). In oat husks these percentages have been studied to be 37,0 % of hemicellulose, 32,1 % of cellulose and 13,7 % of lignin which of course vary by species and by growth conditions (Salo and Kotilainen 1970). Hemicelluloses are polysaccharides as are celluloses but branched and varied in the monomers. Hemicellulose primarily contains following monomers: glucose, galactose, mannose, arabinose, fucose, and xylose with glucuronic acid and galacturonic acid amounts varying by source. Hemicelluloses manage to build up to 100 to 200 sugars per molecule thus being significantly smaller than cellulose in DP as well as physical size by the fact that hemicellulose are branched and amorphous. The hemicellulose's side chains and acetyl groups make it more diverse and less crystalline than cellulose. That's why hemicellulose is more soluble to water and solvents and more chemically reactive than cellulose. Cellulose and hemicellulose both being sugars form hydrogen bonds to each other. Hemicellulose also bonds covalently to lignin and the three of them make up the plant secondary cell walls to fully grown plant cells. With the inclusion of lignin, secondary cells walls become less flexible and less water permeable than the primary cell walls which makes them unsusceptible to rotting. (Gibson 2012)

1.1.3 Lignin

In plants, lignin's function is to harden the cellulose and hemicellulose structure of secondary cell walls. Lignin polymerises in between the cellulose microfibrils and hemicelluloses around them glueing the celluloses together. Lignin is a major contributing factor for rigidity, hydrophobicity, and microbial resistance of plants secondary cell walls. For example, cotton, which is mostly cellulose, is soft, flexible and absorbs water up to 10 times its weight, is very different than wood materials and lignin is the differentiator. Difference chemically is that lignin has filled the space around the cellulose where water would like to make hydrogen bonds. Lignin being a hydrophobic molecule it also repels water molecules around it. (Ek 2009)

Lignin is a polymer consisting mainly of three monomers often also called lignols. They are very similar to each other with phenol being the main structure in all of them. The three lignols precursors to lignin are coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. After linking to a lignin molecule, the lignols are known as p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) respectively. Their differences are the number of methoxy groups attached to the phenol ring, zero, one or two. Relative amounts of the lignols vary in different plant species. Lignols' precursors polymerise making either an ether (C-O-C) or carbon to carbon (C-C) covalent bonds. Lignin crosslinks in very complex ways and does great amounts of branching. (Boerjan et al. 2003).

Softwoods or conifers are cone-bearing seed plants for example pine and spruce. Their lignin consists almost exclusively of coniferyl alcohol also known as guaiacyl, and small amounts of *p*-coumaryl alcohol, named *p*-hydroxyphenyl, in the compression wood. Compression wood adapts to the compression which happens on the sides of the tree, and its lignin content is higher than other areas of the tree. Hardwoods, for example, oak, beech and birch have lignin with coniferyl and sinapyl alcohols in approximately equal amounts. Grassy plants have a different lignin composition again which contains all the lignols, and it is named grass lignin or HGS-lignin for all the three primary lignols. It has more *p*-coumaryl alcohol than wood lignins. This lignin is common in any non-wood plants, but also palm trees and banana-plants which look like wood plants. Lignin content in non-woody plants is much lower (1-20 %) than in woody plant tissues. (Ek 2009)

Because of the monomers all having a phenol with conjugate double bonds, lignin is very colouring compound. The phenol and close by double bonds are called a chromophoric structure. Chromophores are a molecular aromatic structure where carbon to carbon double bonds are close by every other bond. With the double bonds being so close to each other the electrons in those secondary pi bonds are free to travel the area between all the carbons in reach where every second bond is a double bond. The electrons delocalised are stable, they bring aroma and flavour to materials, but also colour. Bleaching makes its effort trying to break or modify these chromophore structures or breaking lignin up to smaller pieces altogether. (Gellerstedt 2009)

1.2 Fractionation

Pulping is a process that extracts the fibrous cellulose material from plant biomass. Chemical pulping methods are mostly utilised with non-wood pulping (Sapuan, Ainun, and Ilyas 2023). Pulping is done to achieve a great cellulose yield for pulp and paper industries, with minimal extra processes. Fractionation processes differ slightly to separate different components, hemicellulose, cellulose and lignin, from the plant biomass (Arzami et al. 2022). Pulping and fractionation together separate the three main components of plant biomass, hemicellulose, cellulose and lignin. (Azeez 2018)

Oat husk and all other plant biomass types can be fractionated to separate their components. For example, oat husks contain 37 % of hemicellulose from dry weight, 32,1% of cellulose and 13,7 % of lignin. Rest of the mass had proteins and ash at 1,4 % and 7,3 % respectively, but not all components were identified. (Salo and Kotilainen 1970). Other biomass types have different amounts of each component with lignin content from 9 % of sisal plant to 31 % of bamboo. Hemicellulose amounts vary from 6 % to 38 %. Amounts of usable long fibre alpha-cellulose vary from 29 % to 68 %. (Azeez 2018)

In fractionation, hemicelluloses are separated first from the biomass using a heating process at around 130 °C (Arzami et al. 2022). Hemicellulose is composed of sugars, amorphous polysaccharides, which include xyloglucans, xylans, glucomannans, and galactoglucomannans. Hemicellulose sugars dissolve easily in hot water whereas cellulose is more strongly bonded and is not impaired by this temperature. Although hemicellulose is not as large a polymer as cellulose but it still contains 500 to 3000 monomers in chains (Gibson 2012).

After removing hemicelluloses, remaining lignocellulosic mass in oat husks typically consists of 50 % cellulose and 50 % of lignin, along with some impurities like ash and proteins (Salo and

Kotilainen 1970). Lignin is a complex aromatic phenolic compound consisting of mainly from three different alcohol monomers called *p*-coumaryl, coniferyl and sinapyl alcohols. Attached to the lignin polymer they produce complex cross-linking (Boerjan et al. 2003). Fractioning lignin away can be done by heating the lignocellulosic mass to temperatures of 155-170 °C in alkaline conditions at over 10,2 pH. In wood pulping, approximately 90 % of lignin is easily dissolved during the pulping process and further delignication of the cellulose is the more difficult and often yield losser and cellulose damage is more prevalent (Suess 2010).

1.3 Bleaching cellulose

Small amounts of lignin is still left in the cellulose mass after pulping or fractionation. To maintain good pulp yield and quality, the remaining lignin amount is usually kept around two to five percent of the pulp (Hart 2019). That's why the material is often called lignocellulosic mass. Fractionation or pulping cannot perfectly get rid of all lignin and that's why bleaching is done to remove more of lignin and its brown colour from the pulp without totally breaking cellulose strands. Bleaching is achieved by modifying lignin's chromophore structures and by removing lignin altogether. Chromophores are a structure in a molecule where electrons are free to move around many carbon atoms, as the atoms have shared secondary pi-bonding. This free movement from electrons gives molecules its colour as the electrons capture light to excite themselves from normal ground state to an excited state. Chromophores in lignin are phenyl groups and connected carbon-carbon double bonds (Suess 2010). When lignin is broken into smaller pieces it is easier to wash away in following steps. Bleaching success is measured with 457nm wavelength light in a TAPPI or ISO standard measurement (Hart 2019). Bleaching is affected by pulp impurities like metal atoms which become metal complexes in pulp and are chromophores which bleaching chemicals react with. Metal and other impurity amounts can be lowered by different pulping parameters and more efficiently by different washing processes after pulping. Acid washing and other treatments after pulping help reduce the amount of metals, because usually the rest of the bleaching stages do not address metal complexes. (Suess 2010)

Bleaching in the pulp and paper industries started with one chemical and a one-step reaction, but after trial it was found that many reaction stages with less chemical can achieve the same bleaching action with more chemical efficiency. A three-stage reaction with three different chemicals became the standard but pulp plants nowadays use several different chemicals in subsequent reactions to bleach their products with washing steps in between. The modern bleaching reactions and procedures are named in a system of letter designations to different chemicals. Most used reactions for example C for chlorine, E for caustic (NaOH) extraction, H for sodium hypochlorite, P for hydrogen peroxide and Z for ozone. These letters are then used in combination as the bleaching reactions advance, for example the old chlorine based bleaching reaction had a name of CEH which meant that pulp underwent three chemical reactions with washing in between. CEH meant chlorine, E for NaOH extraction and the H for sodium hypochlorite. From the 1970's to the 1990's optimisation led to a sequence of CEDED which lessened environmental impact by reducing the need for water and energy. After further process optimisation for cleaner effluent water, the reactions stages were developed to be OD(EO)DD, D(EOP)DD, D(EP)DD or similar variations where new chemicals are O for oxygen, D for chlorine dioxide. With brackets they indicate that the reaction chemicals are more closely applied and/or no washing is done in between the reactions. (Hart 2019)

Differences of bleaching of wood and non-wood products lie in the composition of different plant species. Non-woods usually have a lower lignin amount as percentages go from 18,1 to 28,4 % in the study of (Ferdous et al. 2020). With oat husks there has been study were lignin percentage was 13,7 % and cellulose content 32,1% but comparing values of these two studies might be pointless (Salo and Kotilainen 1970). In Ferdous' study again cellulose amount was good from 29,6 to the highest value of 46,9 % from bamboo. Lower lignin amounts make pulping and subsequent bleaching easier and less costly. The costs of bleaching are lowered compared to wood raw materials. (Azeez 2018)

Pulp bleaching chemicals have three main categories to assess, and they are based on the chemicals used for bleaching. First category is chlorine bleaching which was used for a long period of time but is nowadays banned in many countries. Secondly, elemental chlorine free bleaching where elemental chlorine is not used but other chlorinated compounds are acceptable. Thirdly total chlorine free bleaching where no chlorine is used.

1.3.1 Chlorine bleaching

For the longest time chlorine gas was used in the bleaching process as the main bleaching chemical. It is a powerful oxidiser and modifies the chromophores of lignin to remove its colour. The efficiency comes from the chlorine's specificity against lignin chromophores as using it does not affect cellulose's chemistry much. Chlorine gas is cheaper to use for bleaching against other chemicals derived from it or totally different bleaches. (Hart 2019)

Problem with elemental chlorine in bleaching is its ability to attach into organic compounds making them chlorinated. These molecules are called chlorinated organic compounds and belong to a waste group adsorbable organic halides (AOX), and they often are very long-lasting chemicals because of their slow and difficult degradation. Many AOX have been found to cause cancer, reproductive and hormonal abnormalities. They are also highly toxic and mutagenetic and because of this their release in wastewaters is regulated in many countries. Pulp mills have changed processes as the chlorine's health risks have been seen. (Liu et al. 2018)

1.3.2 Elemental chlorine free bleaching

Elemental chlorine free (ECF) bleaching is a step towards a cleaner bleaching method. ECF bleaching does away with elemental chlorine use but uses other chemicals with chlorine in them for example chlorine dioxide. The amounts of chlorinated organic compounds these chemicals produce is far less than chlorine gas bleaching and do get to the modern effluent emission requirements of many countries. (Hart 2019) For example, in China these AOX emissions should be lower than 12 mg/l in the wastewater, which the ECF bleaching methods achieve. (Liu et al. 2018)

Chlorine dioxide which is a very often used chemical in ECF bleaching. It has a strong oxidation capacity and breaks lignin down into smaller more water soluble molecules (McKague et al. 1995). Chlorine dioxide also attacks lignin's phenol groups which are the chromophore at the centre of lignin's monomers. Phenols in the reaction become free radicals and after several reaction steps lose some double bonds of the phenol's benzene ring to become less colouring. (Liu et al. 2018)

Sodium or calcium hypochlorite ($NaOCl$ or $Ca(OCl)_2$) is a bleaching agent used in pulp and water treatment. It oxidises lignin to remove the colour like hydrogen peroxide at alkaline conditions in Figure 1. Hypochlorite anion (OCl^-) is nucleophilic and cleaves lignin side chains and oxidises quinones into carboxylic acids. Quinones are produced from phenols when a carbon with a double bond –CH= is oxidised to a quinone
–C(=O)– which then go on to be oxidised to carboxylic acids. (Suess 2010)

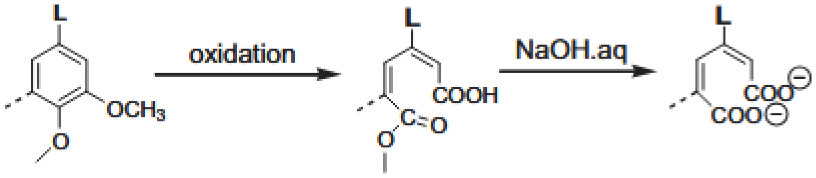

Figure 1: General mechanism of bleaching when breaking lignins chromophore structure. (Ek et al. 2009)

Hypochlorite anion is pH dependent and is in balance with hypochlorous acid. The pH equilibrium is at around pH 9 and below that hypochlorous acid will be the active compound in oxidations. It is a more powerful oxidiser but also does more damage to the alcohol groups of cellulose at the same time. As using hypochlorite, there must be control of pH to achieve wanted results. Below pH 9 will increase the cellulose depolymerisation rate. Hypochlorous acid cleaves carbon to carbon linkages between glucoses. (Suess 2010)

1.3.3 Total chlorine free bleaching

Some Canadian states have banned all AOX waste altogether, but the market has also steered factories to having a total chlorine free (TCF) bleaching method (Liu et al. 2018). It does not utilise any chlorine products in the bleaching stages to eliminate the amount of AOX in their effluent water from bleaching. Bleaches used in TCF methods include oxygen, hydrogen peroxide, ozone and even enzymatic bleaching. (Hart 2019)

Hydrogen peroxide is a bleaching chemical I also used in my bleaching experiments, as it is easily available and commonly used in households. In pulping it is used in the final stages of a bleaching sequence called brightening. Peroxide is used in alkaline conditions as the hydrogen peroxides ion perhydroxyl anion (HOO-) is believed to be the primary actor of bleaching. It needs alkaline conditions around pH of 9.5 and temperatures of 50 to 110 °C. The anion is a strong nucleophile which attacks carbonyl- and conjugated carbonyl-containing structures which are present in pulp as the residual and heavily oxidised lignin. Hydrogen peroxide also works in different ways if it is transformed into hydroxyl radicals (HO•), superoxide radical anions (O2•-) or oxygen. These compounds react indiscriminately with lignin and carbohydrates cellulose and hemicellulose, which quickly affect the cellulose degree of polymerisation and yield. These reactions are not wanted for keeping the yield and degree of polymerisation high. That is why production of the radicals or oxygen are tried to be avoided by removing catalytic compounds hydroxide or transition metals like iron and manganese from pulp before. (Hart 2019) (Liu et al. 2018)

Oxygen bleaching is performed with alkaline conditions, so the broken-down lignin particles are easily washed away in the caustic liquid. Gaseous oxygen is mixed to the solid fibre matrix and alkaline liquid phases. The washing liquid is also recovered to gather dissolved organic material to keep effluent amounts lower and the waste treatment easier. Oxygen delignifies by oxidising residual lignin particles from in between the cellulose fibres which are then easier to wash away. Oxygen bleaching also attacks carbohydrates which affects yield and degree of polymerisation of cellulose. Ozone is a similar non-specific reaction which reacts with lignin, cellulose and hemicelluloses. Its effectiveness against lignin can be improved by reaction conditions like comparatively low temperatures of below 50 °C and a pH of less than 4. Both oxygen and ozone delignification methods are problematic as pH for all pulping steps is in the alkaline side of pH spectra and these would like it to be around neutral or even lower. But both bleaching methods are in use at pulp mills (Hart 2019).

1.4 Applications of oat husk cellulose

Cellulose is used already in food, medical and cosmetics applications. In its various forms it can have multiple useful properties which are utilised in different applications. (Wüstenberg 2014)

Cellulose has multiple properties which are used in the cosmetics applications. With small modifications to the cellulose many different use cases can be covered. Microcrystalline cellulose (MCC) and carboxymethyl cellulose are used similarly in cosmetics products such as emulsions, creams and gels to increase viscosity and improve their stability. Hydroxypropyl methylcellulose (HPMC) is used to form breathable films in facial masks and serums, which keep skin looking moisturised for longer. Cellulose as itself is used as a binder and a bulking agent to keep material to the wanted consistency. Cellulose can be made into beads which can be used as an alternative to solid beads that are used in exfoliating creams. Cellulose also absorbs oil and waxes and therefore is used to mattify skin in cosmetics products. (Wüstenberg 2014)

Similar properties are used in the food industry and cellulose is then often applied. Cellulose is not digested by human gut and can then be added to products without adding calories. Despite having no calories, it has a health benefit as the fibre move nutrients through gut. Cellulose can act as a texturiser or thickener to for example sauces to modify viscosity. Cellulose thickener has also been used when low-fat foods are made as it simulates the mouth feel fat produces. By replacing fat in foods cellulose can be used to achieve low-fat, no-fat or less calorie products and with similar properties for the consumer. Cellulose is also used as an anti-caking agent for example grated cheese to not clump up again. In these uses, cellulose which is from other sources than wood, is more desirable. (Wüstenberg 2014)

1.5 Design of Experiments for bleaching reaction optimisation

As these rection chains had multiple variable parameters to optimise in two stages of bleaching it would be strenuous to do all experiment possibilities and see optimal parameters of bleaching that way. Basic purpose of design of experiments (DOE) is to lessen the amount of human labour needed to get process optimised. DOE is an activity which promises to ease the experiment load by planning the experiments, then afterwards calculating and comparing the experiment end values. In practice a DOE software works by asking for all the variables there are to modify the experiment. The software also wants to know what measurements it is going to get from the experiments and how should they be managed. For example, measuring colour from a reaction, there's a choice of maximising, minimising or targeting a certain value for the colour. After software knows how many parameters can be changed it gives a table of experiments and their different parameters to test out. After experiment completion and measurements, the data is given back to the software to calculate which parameters achieved results and which were not as effective. Software uses statistics and of course its own algorithm to estimate the optimal parameters to meet the criteria user applied.

1.6 TAPPI and ISO and ASTM measuring standards

There are several organisations managing standards for different industries. Pulp and paper industries are not different as they have a more detailed organisation for only pulp and paper but then also other larger organisations which also manage standards for pulp and paper. TAPPI is a worldwide association for pulp and paper industry. It is non-governmental organisation (NGO) working to publish and share scientific articles and new technologies but also to standardise different aspects of pulp and paper industry. ISO is a similar international NGO but focuses more on standardising various industry processes. It has very broad spectrum of standards which cover for example manufactured products, laboratory practises, food, IT and healthcare. ASTM, formerly known as the American Society of Testing and Materials, is a standardisation organisation with the same goals of setting standards for everybody. ASTM is nowadays called ASTM International. From these organisations I have a collection of measurement standards, which are utilised to measure needed material properties.

For the measurements of whiteness of pulp ISO 2469 and the additional ISO 2470-1 and -2. 2469 standardises the way measurement devices are constructed and used to achieve comparable results. ISO 2469 has information about the measurement machine and more precisely the light source, diffusion system of the light in specific ways and specifications for the measuring photometer. The machines, subjects of these standards measure paper or pulp brightness which translates to whiteness of paper. Connecting to ISO 2469 is the following 2470-2 which has specified the types of light sources and wavelengths which should be projected to the test paper. Specifically, 457 nm light is the basis of the ISO 2470 pulp brightness measurement R457. Additionally, they specify a newer standard where along with the blue colour of 457 nm light, some UV light is also projected to the paper for the measurement of R457 D65 to represent light outdoors. (International Organization for Standardization 2024) (International Organization for Standardization 2016) (International Organization for Standardization 2008)

ASTM D 4243 is used to measure cellulose degree of polymerisation. It explains a viscosity measurement with purpose made glassware. Measurement is done with glass capillary device through which goes the freeze-dried cellulose and water solution gravity fed also against capillary forces. The time which the cellulose spends in the glass tube and the amount of cellulose in the solution tells the degree of polymerisation as larger molecules move slower in the tube. Larger cellulose molecules have more difficulty finding space to go through the glass tube and have more hydrogen bonds trying to slow flow and smaller molecules would then flow better. Degree of polymerisation value is also an average value, and cellulose is in longer and shorter pieces as well. Cellulose strands are not conformed to the same degree of polymerisation. (Maraghechi et al. 2023) (ASTM International 2016)

TAPPI T 203 cm-22 for the measurement of alpha cellulose in pulp, which tells us the amount of undegraded, higher-molecular-weight cellulose content in pulp. Beta-cellulose is more degraded and lower DP cellulose and gamma-cellulose mainly consists of low DP cellulose often said to be hemicellulose. Alpha-cellulose is the most stable and therefore most desirable form of cellulose in many applications. A dry 1,5 g measured sample of cellulose is further dried in 105 °C oven and then mixed to a water suspension. This solution is treated with 17,5 % NaOH solution on a glass crucible filter membrane which lets the solution parts with low DP. NaOH solubilises gamma cellulose which will go through the filter, but beta-cellulose may dissolve at first but will not go through the filter and will reprecipitate after the alkali treatment when washing. Washing is done with acetic acid to neutralise alkali and then water. After washing the glass crucible filter is left with the alpha-cellulose and they are dried and again weighed to measure the amount of alpha-cellulose compared to the amounts of solubilised gamma and beta celluloses. (Ritter 1929) (Technical Assosiation of the Pulp & Paper Industry Inc. 2022)

Tappi T 236, Kappa number is for measuring the amount of lignin left in the cellulose sample. Its equivalents are ISO 302. Both work by titration comparison of titration of blank and sample. Sample is weighted and ultrapure water is added. 50 ml of 0,1 M $KMnO_4$ and 50 ml of 2 M H_2SO_4 is added to the sample solution. 10 ml of KI is also added and then titrated with 0,2 M $Na_2S_2O_3$ which turns sample first to yellow after which starch is added to achieve a dark colour. Then titration is continued until dark colour turns to white or colourless. Process is the same for the blank but without the sample and these values are compared after some calculation. (Technical Assosiation of the Pulp & Paper Industry Inc. 2013)

Many of the ISO, ASTM and Tappi measurement standards are very similar to each other as they try to achieve a similar measurement value for samples. Being similar they aren’t always the same and quite large differences can be found, as is the case with the brightness measurements. Comparing the different standards of ISO 2469, 2470 and Tappi T 452, Brightness of Pulp, Paper, and Paperboard. The purpose of all of these is to standardise the measurement of brightness. Standards provide an instruction for measuring pulp’s paper sample reflectivity which can be compared to a calibration sample. The differences start from the light source. In TAPPI system the light source is shone to the paper in a 45 ° angle and photoreceptor is at 90 ° and perpendicular to the paper. In TAPPI measurement light will go to the receptor in different amounts if paper is smoother or rougher. Reflection amount would be different depending on the topography and surface of the paper. In ISO standard the photoreceptor is similarly positioned but the light source has a more elaborate system where a void above the paper is lit up by the light source. The light is then coming to the paper from all angles and directions which the TAPPI system does not consider. This lighting will more easily get closer values from a rougher and a smoother paper. Light source differences continue as TAPPI 452, and older ISO 2470-1 uses a light source of pure blue light at 457 nm which correlates well with whiteness for human eye as usual brown and yellow pulp materials absorb this wavelength. It is denoted as R457. ISO 2470-2 use again a 457 nm wavelength of light but also mix in UV light which simulates the paper in typical outdoor lighting. This advancement is denoted by R457 D65. (International Organization for Standardization 2024)

1.7 Objectives of the experiment

Cellulose is a useful component in different products as it has beneficial properties and effects. In this experiment we want to further advance the product development of oat husk cellulose by bleaching it. Bleached cellulose would be easier to use in products as the colour would not be affected by the brown lignin.

Experiment contains small-scale bleaching reactions with sodium hypochlorite and hydrogen peroxide with varied reaction parameters. With differing parameters, an optimal bleaching reaction would hopefully be found to achieve brightening of the oat husk cellulose but keeping the cellulose degree of polymerisation high. Bleached samples are measured for brightness and degree of polymerisation of cellulose with some additional kappa number and alpha cellulose measurements.

With these measurements we can estimate how the bleaching reactions affect amounts of lignin and amounts and condition of cellulose.

Objectives for the experiment were to achieve bleaching reactions in a small scale, to achieve varying results from the bleaching reactions and to compare the results by different measurements. Lastly achieving enough knowledge to optimise the bleaching reaction for this raw material.

2 Materials and methods

2.1 Oat husk fractionation and cellulose preparation

Oat husk cellulose was fractionated in the CH-Bioforce 2000 litre reactor. In the tank cellulose was acid washed for removing metals and treated with lye to neutralise the material. After reactor stages 25 litres of lignocellulose mass was washed with reverse osmosis (RO) water to remove colour and some lignin. Cellulose was pressed in seven batches in a metal basket to remove excess water. Lignocellulose was then mixed and bagged in one litre re-closable plastic bags to have 25 g of dry cellulose which was 79,8 g wet mass at its 31,32 % dry content. 250 ml of RO-water was added to all bags to achieve same consistency in other words dry content % to all bags.

Design of experiments software JMP was utilised to guide the experiment. JMP custom design was used. Five different factors were applied for the software. Hypochlorite reaction factors were hypochlorite dosing from 0 to 2 % in 0,5 increments and reaction temperature from 20 to 40 °C in 5 °C increments. Hypochlorite dose 0 % is locked in software to be 20 °C reaction as nothing is done for 0 % dose. Then similar factors were applied for the hydrogen peroxide reaction, but dosing from 0,5 to 2 % and temperatures from 40 to 80 °C now with 10 °C degree increments, with additional factor of hydrogen peroxide reactions starting pH from 10 to 11,5 with 0,5 pH increments. These add up to five factors and 23 settings in them for the reaction chain. Responses were applied to the software as following. Degree of polymerisation of cellulose, ISO whiteness value, alpha-cellulose and kappa number, and from the values of these responses, software calculates following experiment steps and optimisations. JMP software suggested 25 sets of experiments with following settings showed in Table 1, which were completed.

Table 1: Bleaching parameters for the experiment
Bleaching parameters from the design of experiments software JMP. Reaction bleaches are NaOCl, sodium hypochlorite and H_2O_2, hydrogen peroxide

Bag No.	NaOCl DOSE (w-%)	NaOCl TEMP (°C)	H_2O_2 DOSE (w-%)	H_2O_2 TEMP (°C)	H_2O_2 pH
1	0	20	0,5	80	11
2	1	30	1,5	80	11,5
3	2	25	1	60	11,5
4	2	35	1,5	50	10
5	1,5	25	2	80	10,5
6	1	25	1,5	40	10
7	2	30	2	40	11
8	1,5	30	0,5	70	10
9	0,5	40	1,5	40	10,5
10	1	20	2	50	11
11	1,5	35	1	40	11
12	1	35	0,5	60	10,5
13	0,5	35	2	70	11,5
14	1,5	40	2	50	11,5
15	1,5	20	1,5	60	11
16	0,5	30	1,5	60	11
17	2	20	1,5	70	10,5
18	0,5	30	1	50	10,5
19	0	20	2	60	10
20	0	20	1	50	11,5
21	1	40	1	70	11
22	0,5	20	0,5	40	11,5
23	0,5	25	0,5	50	11
24	2	40	0,5	80	10
25	0,5	20	1	80	10

Bagged cellulose underwent 60-minute reactions in a Julabo 20B water bath with Thermo Scientific Haake DC10 temperature controller and water circulator. Reagent doses were calculated in weight-% of the 25 g of dry cellulose. Hypochlorite was titrated to be at concentration of 10 % by iodine and sodium thiosulfate titration. Density was measured to be 1,25 g/ml so dosing 0,5 % is 1 ml of hypochlorite solution. Hydrogen peroxide was a 30 % solution, with a density of 1,11 g/ml therefore measures a 0,375 ml volume as a 0,5 % dose. Dosing was done into the re-closeable bag and mixed by hand through the bag and then put into the water bath. Bags were mixed by hand every 10 minutes for the duration of one hour. After a completed reaction batch cellulose samples were washed with RO water in a 25 µm filter mesh to not lose fibre in the washing. Fibre was then packed back into re-closeable bags with added RO water which was lost in washing. The reactions were done in batches for each temperature. Hydrogen peroxide reactions' dosing and temperature were done in a similar way, but the temperature range was higher at 40 to 80 °C. The hydrogen peroxide reaction had also the pH measurement which was achieved by adding NaOH 1 % solution incrementally and measuring with a Thermo Scientific Eutech Elite pH meter. After pH was set for all bags in the batch, the bleach dosing was done, and bags were put in the water bath. Hydrogen peroxide reaction was also 60 minutes, and washing was done after that.

2.2 Measurement of cellulose degree of polymerisation

Once the reactions were complete, measurements were started. Degree of polymerisation measurements were done from a sample of the pulps which were freeze dried to remove moisture. Samples' dry contents were measured and then around 0,180 g of sample was weighed into plastic bottles for the first round of DP measurements. 25 ml of RO water was then measured into each bottle and mixed well to not have cellulose clumps. 25 ml of copper ethylenediamine solution was pipetted into bottles and mixed for 15 minutes in an Edmund Bühler KS 15 circular shaker. The bottles of sample were squeezed to remove air from the bottle and put into 25 °C Grant TC120 heated circulating water bath. After 15 minutes in the water bath samples were one by one put through the DP test which consists of putting the solution into a beaker and sucking the sample into a DP measurement device tube with a vacuum pipette. Measurement is based on the time it takes for the solution to flow through the measurement device tube with gravity (ASTM International 2016). Acceptable measurement times are from 60 to 100 seconds. If the result falls outside this time range, a new cellulose sample is prepared and measured in a new bottle. The amount of cellulose and the dilution used, compensate for the sample's DP and therefore influencing the evacuation time. Both time of the evacuation and amount of cellulose measured are used to calculate DP value.

2.3 Measurement of pulp whiteness

Around 80 g of wet bleached pulp was measured into a 2-litre beaker and 1 litre of RO water. Contents are mixed with a magnet stirrer for 10 minutes and then poured into a Lorentzen & Wettre F 101 paper machine and then mixed with bubbles. After three seconds of settling, the water is released through the sieve which keeps the pulp on top and makes the paper. Paper is then dried with drying papers which are stacked on top and a metal plate at the top. Then rolled for 20 seconds with a heavy roller to extract water through the sieve and into the drying papers on top. After second and third time of rolling, the paper is dry enough to handle and can be set to air dry in a 50 % humid room at 25 °C in between two drying papers. After drying for 24 hours, the paper is dry and can be stored in dark to avoid yellowing of paper. Paper whiteness is measured from three points on each side of the paper to get an average value of brightness with Lorenzen & Wettre ELREPHO with settings of R457 D65 referencing to ISO 2470 (International Organization for Standardization 2008).

2.4 Measurement of alpha-cellulose

This measurement is gravimetric, so the used glass filters are weighed and marked for each sample. 1,5 g of dry cellulose is measured into 400 ml beaker. Water bath is heated to 25 °C and 17,5 % NaOH solution is put to warm up in water bath with 100 ml of RO-water for samples. After warming up 30 minutes 100 ml of 17,5 % NaOH is measured into a measuring glass and 60 ml of it is poured to the sample beaker. Start a timer for 60 minutes during pouring. Sample is then stirred with a glass rod and if sample does not become homogenous, an immersion blender is used to mix pulp sample into NaOH. Rest of the NaOH, 40 ml, is used to rinse all pulp material from the blender to the solution not to lose material. Solution then gets a lid and is put into water bath for 30 minutes, when 100 ml of RO-water from measuring glass in water bath is mixed in and stirred. After the 60 minutes has passed, sample solution is transferred into a 150 ml SCHOTT filter crucible with a porosity of 2, placed above a 250 ml SCHOTT glass suction flask. If possible, the pulp NaOH solution is filtered without applying suction, then the resulting filtrate is filtered once more. Glass filter crucible is then transferred from the 250 ml flask to a 3000 ml suction bottle and 625 ml of RO-water is filtered through. After water filtration vacuum away moisture from the pulp and pour in 100 ml of 20 % acetic acid and let filter under lid for 5 minutes and vacuum filter dry again. Then filter through 1000 ml of boiling RO-water with vacuum help if needed and vacuum filter dry. Glass filter crucible can be then put onto a 250 ml decanter and transferred to a 105 °C oven to dry overnight. Dry glass filters are cooled in a desiccator for two hours and then glass filters and cellulose on top is weighed and compared to the original filter weight and sample weight to get the alpha-cellulose amount remaining on the filter (Technical Assosiation of the Pulp & Paper Industry Inc. 2022).

2.5 Measurement of kappa number

Measurement is done first with a blank and only then a sample. Blank solution is done by measuring 380 ml of ultrapure water into a 600 ml beaker and then a magnet is added. Beaker is put into a 25 °C small water bath with a lid and a weight on top and let temperature rise to 25 °C. 50 ml 0,1 M $KMnO_4$ and 50 ml of 2 M H_2SO_4 is measured into a 250 ml beaker and added into sample solution. Rinse 250 ml beaker with 20 ml of ultrapure water to the 600 ml beaker. Total volume should be 500 ml. Water bath is put on a magnetic mixer base and beaker in the water bath so mixing can be done. As H_2SO_4 is poured into solution a 10-minute timer is started. Mixing is strong and the bottom of the beaker can be seen. 10 ml of 1M KI is measured into a measuring glass and is covered with foil and put to water bath. When exactly 10 minutes has passed, KI is added to the sample solution. Titration is done immediately with 0,2 M $Na_2S_2O_3$ and magnet mixing. When titration turns colour to yellow, starch solution of 2 g/l is added to make solution very dark. Then titration is continued until dark colour is removed and sample solution becomes colourless or white. With the blank solution the titration amount should be around 25 ml.

Pulp dry content was measured with a Mettler Toledo moisture analyser and amount of pulp needed for the analysis is calculated from an equation. Sample pulp kappa number is estimated to be 1-5 or 5-100 with comparing brightness to previous samples if you can. If kappa is 5-100 the KMnO4 is added like in blank and less water is added. If kappa is thought to be low 1-5 then amount of potassium permanganate $KMnO_4$ is lowered to 25 ml and 25 ml of ultrapure water is added as follows. Sample is measured into a 600 ml beaker with 300 ml of ultrapure water and mixed with a glass rod or handheld immersion blender, if needed. Glass rod or blender is rinsed with 100 ml of ultrapure water to the sample solution. A magnet is added, and beaker is put into a 25 °C water bath with a lid and a weight on top and let temperature rise to 25 °C while magnet is mixing. 25 ml 0,1 M $KMnO_4$ and 50 ml of 2 M H_2SO_4 is measured into a 250 ml beaker and added into sample solution. Rinse 250 ml beaker with 25 ml of ultrapure water to the 600 ml beaker. Total volume should be 500 ml. Beaker was put on a magnetic mixer base for 10 minutes as mixing was strong, where you could see the bottom of the beaker. 10 ml of 1M KI was measured into a measuring glass and was covered with foil. When 10 minutes had passed, KI was added to the sample solution. Titration was done immediately with magnet mixing. When titration turned colour to yellow, starch solution of 2 g/l was added to make solution very dark. Then titration was continued until dark colour was removed and sample solution became colourless or white.

Differences of sample preparation if kappa is 5-100 are the amount of potassium permanganate and less water. As pulp is measured to the beaker, 300 ml of ultrapure water is added to the sample and mixed with a glass rod or blender, which are rinsed to the sample solution with 80 ml of ultrapure water. A magnet is added, and the solution is moved to the water bath and mixed to reach 25 °C. This time 50 ml 0,1 M $KMnO_4$ and 50 ml of 2M H_2SO_4 are added to the solution and 10-minute timer is started. After 10 minutes, the 10 ml of 1M KI is added to the solution and titration is started immediately and continues similarly than in the 1-5 sample and blank sample.(Technical Assosiation of the Pulp & Paper Industry Inc. 2013)

3 Results

3.1 Results from bleaching action

Oat husk cellulose was bleached with a small batch bleaching setup where multiple bleaching reactions could be done simultaneously in re-closeable bags in a single water bath. Bleaching was a two-stage reaction where sodium hypochlorite was the first bleaching chemical and hydrogen peroxide was the second with a washing step in between. The two reactions got five parameters to optimise: bleaching chemicals’ dosage and reaction temperature for both reactions with an additional parameter of pH in the hydrogen peroxide reaction. Bleaching reaction effectiveness was measured with DP measurements and pulp brightness measurements with additional kappa and alpha-cellulose measurements to confirm brightness values as removing lignin.

Bleaching of the first set of 25 samples was successful but process took a lot of time due to both the reaction duration and also the extensive washing required to remove the residual bleaching chemicals. No major problems happened but processes will be discussed individually later. Table 2 shows all the reaction parameters and the measurement results of the first round of bleaching. The ISO brightness column demonstrated that the sample 24 achieved the highest brightness value of 63,98 which is still below the target of 85, but a significant portion of the DP is retained in this sample. Values for unbleached pulp measurements are not on the chart but its ISO brightness of 35,36 shows that all pulp samples have gone through some brightening. Unbleached pulp DP value was 1524 which also shows that some damage was done to the cellulose but not much from all the reactions.

Table 2: Bleaching parameters
Bleaching parameters and results from the experiments of first round of bleaching of 25 oat cellulose samples.

Bag No.	NaOCl DOSE (w-%)	NaOCl TEMP (°C)	H2O2 DOSE (w-%)	H2O2 TEMP (°C)	H2O2 pH	DP	ISO Brightness	Alpha-cellulose	Kappa
1	0	20	0,5	80	11	1488	38,08	103,7032	
2	1	30	1,5	80	11,5	1323	48,98		
3	2	25	1	60	11,5	1147	57,35		
4	2	35	1,5	50	10	984	60,74		
5	1,5	25	2	80	10,5	1191	55,84		
6	1	25	1,5	40	10	1423	47,05		
7	2	30	2	40	11	1118	57,94		
8	1,5	30	0,5	70	10	1212	54,67	102,559	5,4
9	0,5	40	1,5	40	10,5	1417	40,59		
10	1	20	2	50	11	1277	50,88		
11	1,5	35	1	40	11	1118	56,34		
12	1	35	0,5	60	10,5	1328	46,21		
13	0,5	35	2	70	11,5	1417	43,44		
14	1,5	40	2	50	11,5	1144	56,57		
15	1,5	20	1,5	60	11	1311	51,37		
16	0,5	30	1,5	60	11	1478	40,52		
17	2	20	1,5	70	10,5	1207	56,73		
18	0,5	30	1	50	10,5	1448	40,16		
19	0	20	2	60	10	1494	37,59	102,638	14,2
20	0	20	1	50	11,5	1486	37,72		
21	1	40	1	70	11	1311	46,72		
22	0,5	20	0,5	40	11,5	1489	40,89		
23	0,5	25	0,5	50	11	1474	40,34		
24	2	40	0,5	80	10	905	63,98	101,038	3,1
25	0,5	20	1	80	10	1436	40,74		

3.2 Comparison of bleaching chemicals

Seeing from the brightness and measurements in the Figure 2 A&B, the comparison of bleaching chemicals heavily favours sodium hypochlorite. It was the key to bleaching our material with these parameters. Graph in figure 2A shows how linearly the amount of sodium hypochlorite makes pulp brighter, but we can’t see the same at all from hydrogen peroxide. On the hydrogen peroxide chart (Fig 2B) higher dose does not seem to achieve more brightness as only blue grouping achieves a rising curve. Experimentation should be continued with higher doses and temperatures until reaction parameters have been found where DP value drops off significantly. Then from there we would know which temperatures or doses should be avoided with the bleaching reaction to achieve a target DP and enough brightness.

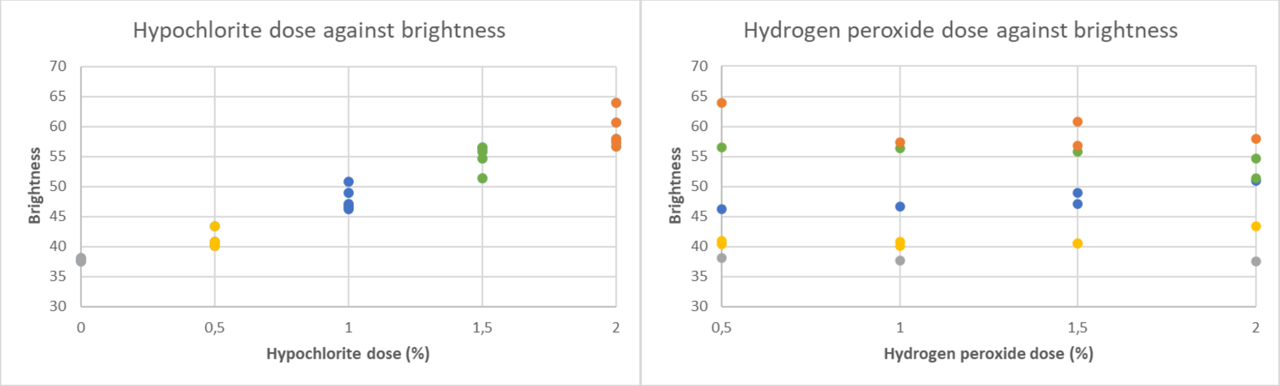

Figure 2A & 2B: Comparison between the effect of dosing two bleaches, sodium hypochlorite and hydrogen peroxide. y-axis is the brightness of the paper made from pulp and on x-axis you see the dosing of each bleach. Colours are representative of hypochlorite dosing amounts.

Cellulose degree of polymerisation did correlate with the brightness of pulp as is shown in Figure 3. The more bleaching was done the more damage to the DP was done, by the bleaching chemicals.

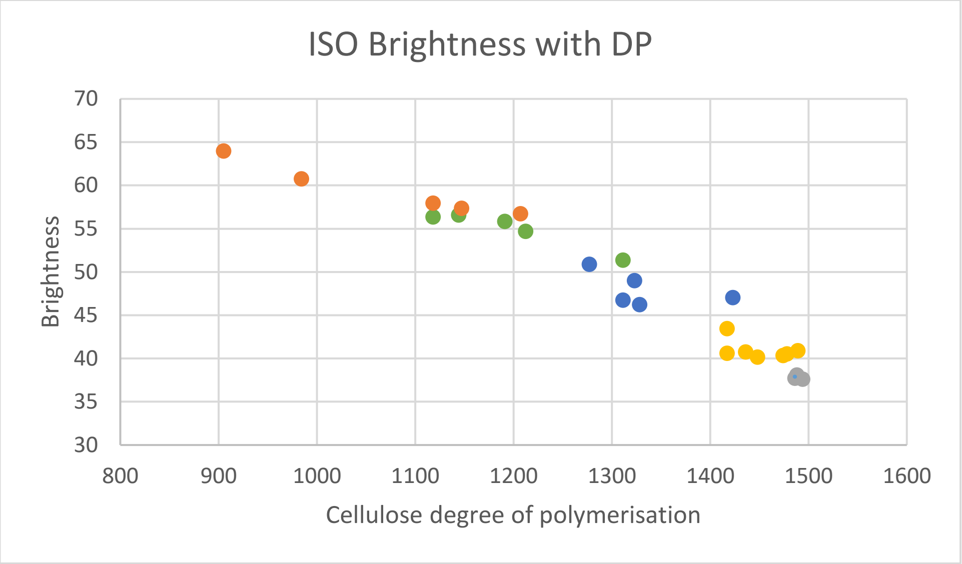

Figure 3: ISO brightness measurement with cellulose degree of polymerisation. Colours are representative of hypochlorite dosing in bleaching: Grey group of 0 %, yellow 0,5 %, blue 1 %, green 1,5 % and orange 2 % dose.

First round of bleaching reactions might have been compromised by not using RO-water in the mixing of cellulose in the bags but was tested in a second round. RO-water was meant to be used but no there is no recollection if RO-water was used. Normal tap water would have metal ions which have a reducing effect to the bleaching action as bleaching chemicals also react with metal molecules. To confirm or deny usage of RO water, a second round of bleaches were done to evaluate if there would be a difference between brightness of first and second round bleaching in similar settings. The second round did the same reactions but did not achieve brighter pulp after the sodium hypochlorite stage. This second test round confirms that RO-water was used or the amount of metal ions in water for the pulp is negligible. After the first bleaching reaction, pulp was washed with RO-water and therefore it wouldn’t affect the second bleaching reaction in the same way.

Most bleaching reaction chains have a step of lye extraction after a proper delignifying bleaching step is made. Bleaching chemicals like sodium hypochlorite works well to break down lignin’s chromophores and breaking lignin into smaller molecules. In the results we may have seen only the results of bleaches breaking the chromophores because we did not use a lye extraction step in our bleaching reaction chain. Lye extraction is meant to remove broken down lignin particles more effectively as part of the washing step. There is a possibility of lignin being broken down to smaller pieces, but washing was not effective enough to remove the pieces of lignin from the pulp. Kappa measurement will tell us more if the samples contain lignin more than the colour suggests as we can compare colour to previous samples which were tested for kappa lignin as well. Results of bleaching may have been different if lye extraction was not off my experiment plan.

3.3 DOE as a hurdle in the experiment

Shortcoming for the use of DOE software can be boiled down to the lack of test runs prior to locking the bleaching parameters up and setting up DOE with these parameters to a quite large set of tests. The values of DP now achieved are higher than needed and product could be much whiter than it was with these locked reaction parameters. Dosages or temperatures could have been much more aggressive to get samples which could have been ruined in DP. That would have given a spectrum of values from all around the optimal range and would have given much more information and have eased the following rounds of testing. After the numerous first batch of experiments and the measurements, time was run out to optimise reactions much further and only a few more runs could be managed in time.

3.4 Importance of different measurements

Main measurements done after the bleaching were the DP, brightness of the pulp measurement, alpha-cellulose percentage, and kappa number measurements. From these measurements the DP and brightness measurements were the most important with keeping cosmetics and food applications in mind. The targets for these values were a DP of 300 or above and a priority of brightness of ISO 85 or above. Targets were set to place where we know product would be interesting in the market for cosmetics and food. The DP of 300 is at the longer end of a product material called microcrystalline cellulose which is used for food and pharmaceutical applications (Rojas 2016). Brightness target was set to ISO value of 85 or above which is a solid white colour to the eyes. ISO 85 cellulose would be suitable for mixing with other white materials and not to colour the end product at all. From the start our oat husk pulp had an ISO brightness of 35,36. Targets for these pulp bleaching measurements were set well, but we overestimated the amount of bleaching our bleaching parameters would achieve and the amount which the cellulose would degrade from the bleaching.

3.5 Comparison of sodium hypochlorite bleaching reaction parameters

Pulp bleached well from the first sodium hypochlorite reaction. Depending on the reaction dose and the temperature, the bleaching did what was expected. From the original brown pulp colour the bleaching reaction removed colour, on less strong reactions, to a lighter brown colour, but in stronger bleaching reactions to a light yellow. Colour removing reaction could be seen happening during the first 40 minutes of the hypochlorite reactions and after that not much happened.

Hypochlorite reaction can be seen with its two parameters on a y-axis of brightness in Figure 4. With dosing, the brightness rises linearly (Fig 4A) but with the temperature this does not happen (Fig 4B). Some upwards trend from temperature rise could be seen on orange and maybe green groups, which are the hypochlorite reactions with dosing of 2 and 1,5 %. Other groups did not seem to have upwards trend in this temperature range. Other factors must be considered to explain the hypochlorite bleaching irregularities.

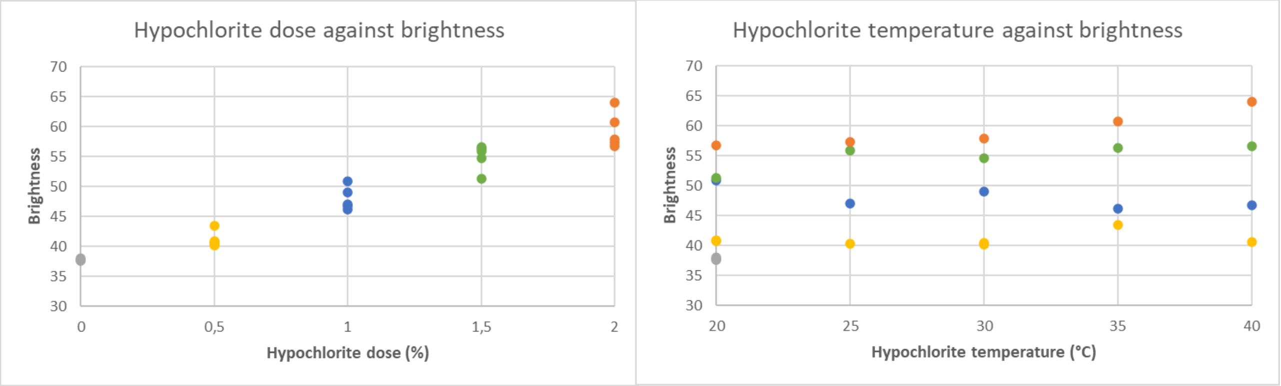

Figure 4A & 4B: Comparison of the effects of dosage of sodium hypochlorite and the reaction temperature on brightness. Colours are representative of hypochlorite dosing in the reaction: Grey group of 0 %, yellow 0,5 %, blue 1 %, green 1,5 % and orange 2 % dose.

In the beginning, bleaching could be well seen to be somewhat localised as mixing was not easy to do in the bag. The amount of bleach also being so little that it didn’t mix easily in a viscous pulp. With the second mixing at the 10-minute mark, localisation of the bleaching could be seen and removed by mixing enough. After hypochlorite reaction, washing was done with a 25 µm filter mesh with RO-water to wash away all chemical residues to not affect pulp anymore in storage. During these washings some pulps washing water did appear to have some colour, removed from the pulp and going through the filter mesh.

3.6 Comparison of hydrogen peroxide bleaching reaction parameters

In the hydrogen peroxide reaction, differences of bleaching were harder to compare by eye as the hydrogen peroxide reaction is the second reaction of the process. All pulp bags are different shades of brown and yellow already in the start, so following bleaching effects by eye is more difficult. Hydrogen peroxide also being the less powerful and slower in its action did it more difficult. Figure 5 shows hydrogen peroxide dose and temperature effects of brightness. Colour groups should have some coherent downward or upward action to consider valuable results. In the dose chart (Fig 5A) we can see positive upward curve in the yellow and blue groups, which represent sodium hypochlorite dosing of 0,5 and 1 % respectively. Effects of temperatures (Fig 5B) in the hydrogen peroxide reaction are difficult to find. Groups are not trending upwards or downwards, and no maximum effectiveness temperature can be seen. Looking at samples which didn't go through sodium hypochlorite bleaching, grey group, did not achieve strong bleaching in any conditions. Differences could be still found in the pH which is in Figure 6. Other aspects which achieve differences in this reaction might need to be found outside our reaction parameters or totally different aspects of the reactions.

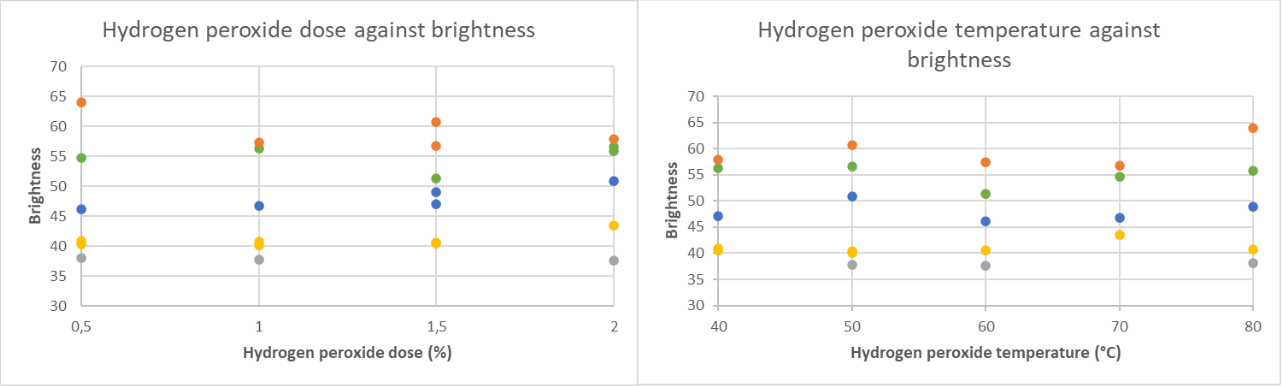

Figure 5A & 5B: Hydrogen peroxide reaction conditions effects on brightness. Colours represent sodium hypochlorite dosing amounts: grey group of 0 %, yellow 0,5 %, blue 1 %, green 1,5 % and orange 2 % dose.

Hydrogen peroxide reaction pH was measured from the pulp before the reaction and not anymore after that. Measurement of pH was a little difficult to manage which might bring in variability to the results. Again, no obvious effects that some pH must be better than others can be seen from Figure 6, but more on that in the discussion section. In the group which did not go through sodium hypochlorite reaction not much differences can be seen in brightness even as they got varied doses of 0,5; 1 and 2 %. Lowest dose was combined with the highest temperature of 80 °C and pH of 11, 1% dose was at 50 °C and highest 11,5 pH and 2 % dose was combined with a temperature of 60 °C and pH of 10. In the end brightest of them was the lowest dose, highest temperature with pH of 11 at brightness of 38,08. Other reactions were very close at 37,72 of dose 1 % at 50 °C and 11,5 pH and brightness of 37,59 of dose 2 % at 60 °C and 10 pH. Results are very close to each other, but bleaching had happened with only the hydrogen peroxide reaction in each bag of pulp from the starting brightness of 35,36.

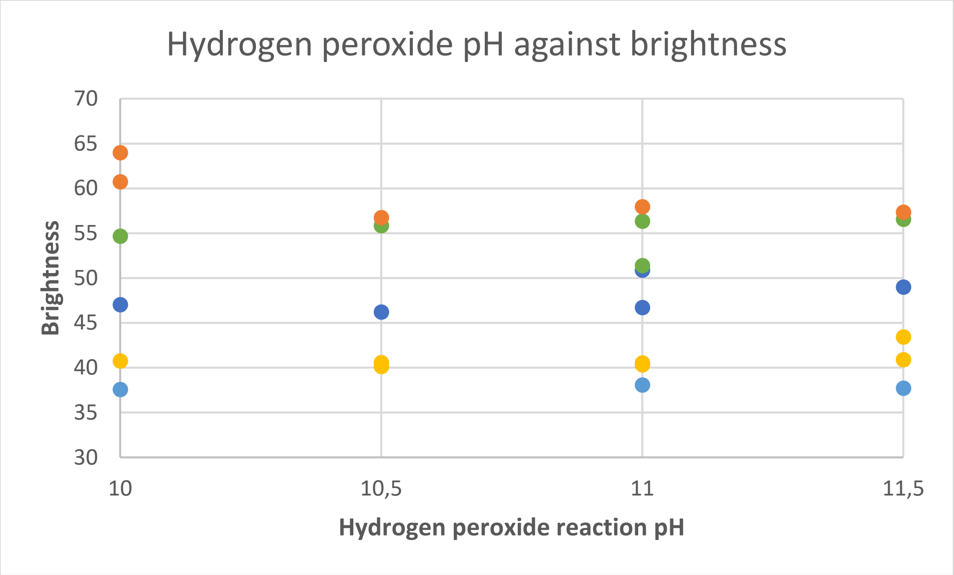

Figure 6: Hydrogen peroxide reaction pH effects on brightness. Colours represent sodium hypochlorite dosing amounts: grey group of 0 %, yellow 0,5 %, blue 1 %, green 1,5 % and orange 2 % dose. .

3.7 Results from the ISO brightness measurement

Measurements of the ISO brightness contain making a paper out of the pulp material. With the only target of the paper being the brightness, paper thickness is not a substantial factor in the measurement. Only too thin of a paper has been tested to affect colour measurements as it lets light through. In standard procedure, paper is aimed to be 200 g/m^2, but our testing being for colour and not strength, papers were made to approximately 240 g/m^2. Papers were all made with around 78 g of wet pulp of 8 % dry content which made a 16*16 cm square. Papers were tested with a light blocking layer of paper underneath to get absolutely no light through, but it did not make a difference, so papers were good enough to measure from.

ISO brightness measurements are done six times on one paper and averaged out to achieve a representative number for brightness. Representative papers are seen in Figure 7, which explains the need for six measurements as you need to find an average of the colour and some single measurements could be affected by the paper inconsistency.

In bleaching reactions, the number of dark spots was lessened, but never with my bleaching system did I get a consistent paper colour which wouldn't have any dark spots. The dark spots of the paper look to be fibre bundles where more colour is stored. Bleaching reactions affect all the pulp fibres in similar level. As pulp has darker and brighter fibres in it, the bleaching does brighten them all by the same amount which keeps the differences of fibre colour in view. Pulp also had knots of some kind which didn't ever break down and stayed very dark as bleaching chemicals didn't penetrate the inside of the knots.

Figure 7: Example of papers which were measured with ISO brightness meter. On the left photo paper is from unbleached pulp.

3.8 Results of the degree of polymerisation measurement

Degree of polymerisation measurements had no anomalies. The results were linear and at least to the eye correlated to the colour of the pulp inversely. As the pulp got lighter the sample cellulose DP value got lower. When lighter pulps were measured the viscosimetric measurement went faster through the tube than darker less bleached pulps. The more bleached pulps had sustained damage to the cellulose during the reactions. Highest values of DP were from the samples which did not go through the sodium hypochlorite reaction with values of 1488, 1494 and 1486. Highest DP was a reaction which got in the hydrogen peroxide reaction a 2 percent dose with a 60 °C temperature and a low pH of 10. Lowest DP was a value of 905 with the highest brightness sample which was 63,98.

Degree of polymerisation correlates with the ISO brightness with all our reaction parameters. Figure 8 shows the correlation, which is strong with a R^2-value of 0,9368 with this group of measurements. The solid line represents the whole groups trendline as the dotted lines are each colour groups trendlines. Groups are divided by the sodium hypochlorite dosing percentage.

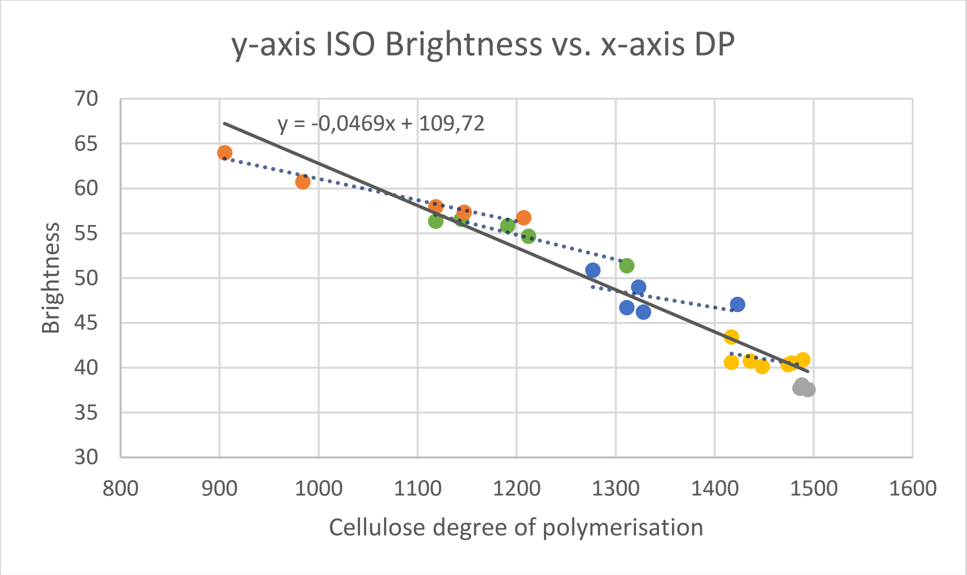

Figure 8: ISO Brightness values versus degree of polymerisation values. Colours represent hypochlorite dosing percentages: grey group of 0 %, yellow 0,5 %, blue 1 %, green 1,5 % and orange 2 % dose. Solid line is the trendline of all points and the equasion is for the solid line. Dotted lines are groups' trendlines.

3.9 Measurement of alpha-cellulose

Few measurements of alpha-cellulose were done to estimate the amount of long and short cellulose strands in the samples after the bleaching (Table 2). Alpha cellulose percentage could tell us if the bleaching has broken cellulose down to smaller pieces along with the degree of polymerisation measurement. Difference being that alpha cellulose can tell us the amount of short and long fibres as degree of polymerisation gives the sum of all fibres which give sample its viscosity. Tests were performed to four samples representing different bleaching conditions and therefore brightnesses too. Samples 1, 8, 19 and 24 were tested with a standard measurement for alpha-cellulose. Samples have had very different sets of reactions. Sample 1 had a sodium hypochlorite dose of 0 %, continuing with a hydrogen peroxide dosage of 0,5 % at the temperature of 80 °C and pH of 11. This sample had one of the highest values of DP and one of the lowest brightness from our tests. Second sample was the number 8 with a hypochlorite reaction from the opposite end of the parameters with dose of 1,5 % and 30 °C but then similar hydrogen peroxide reaction sample 1 with dose of 0,5 % and temperature of 70 with pH of 10. Next sample for alpha-cellulose measurement was sample 19 again with no dosing for hypochlorite to compare if hydrogen peroxide amount would have a major impact. Then sample 19 had a peroxide dose of 2 % with 60 °C reaction temperature and pH of 10. Lastly sample 24 with our brightest colour with reaction parameters for hypochlorite at 2 % dose and 40 °C and then for peroxide 0,5 % at 80 °C at pH of 10.

Difference in alpha-cellulose amounts were minute, but not nothing. Finding correlation from alpha-cellulose measurement to any of the bleaching parameters might be possible. Sample 1 had the mildest doses of bleaches in its reactions in the group, and it has the highest value of alpha-cellulose in it. Sample 8 and 24 had a high hypochlorite dose of 1,5 % and 2 % and low hydrogen peroxide dosage 0,5 % and their alpha-cellulose amount could be reflective of that difference. As hypochlorite reaction is a little weaker, it will not affect cellulose as much and will not break cellulose the amount that higher dose did. Then in the peroxide reaction doses were similar and the difference of alpha-cellulose was kept. Comparing the sample 8 and sample 19 bleaches, that are completely different dosage but, in the end, come up to about the same value in the alpha-cellulose amount. As sample 8 had a stronger hypochlorite reaction, alpha-cellulose was reduced more than in sample 19. But in the next reaction sample 19 did a stronger hydrogen peroxide reaction, which reduced the alpha-cellulose concentration back closer to sample 8 which had a weak peroxide reaction.

As the alpha-cellulose measurement is a gravimetric measurement with small sample amounts it needs the cleanest and most accurately measured glassware and sample, but still differences in measurements were miniscule. Sample 1 alpha-cellulose percent was 103,7% the highest of the group, samples 8 and 19 had similar results of 102,56 % and 102,64 % and the sample 24 had an alpha-cellulose percent of 101,0 %. Values of alpha-cellulose a little over 100 % are not uncommon as usually our fractioned samples have very little to no hemicelluloses to easily filter out in the measurement and gravimetric measurements are very sensitive. Before the end weighing, samples are dried in the oven and then cooled in dry conditions which should keep samples dry but as samples are measured, moisture from the air will absorb into dry sample cellulose material.

3.10 Measurement of kappa number

Kappa number is a value which correlates to the amount of lignin in the pulp and therefore the colour of the pulp and brightness (Figure 9 & Table 2). The more lignin is present in the pulp the darker it is and gets a lower brightness value, and at the same time a higher kappa value. Kappa values were not measured from all samples, but a group with significance. Bleached pulps of 8, 19, 24 and the unbleached pulp were measured with the results of 5,4; 14,2; 3,1 and 16 respectively. Kappa number can be converted to a lignin percent by multiplying with a factor of 0,17 and lignin percents from the pulps are measured to be 0,918 %; 2,414 %; 0,527 % and 2,72 % respectively. The samples 24 and 8 were the brightest of the group and the kappa number correlated to be the lowest with values of 3,1 and 5,4 respectively. The amount of lignin left in the pulp is negatively correlating to the brightness of the pulp which can be seen from the Figure 9. The differences of unbleached pulp and the pulp number 19 with low efficiency bleaching is relatively larger in the kappa number than in brightness. There a large amount of lignin has been removed but still the brightness changes very slowly. In the other end, the amount of lignin removed between pulps 8 and 24 is like the difference of the other pair, but the amount of change in brightness value is much larger.

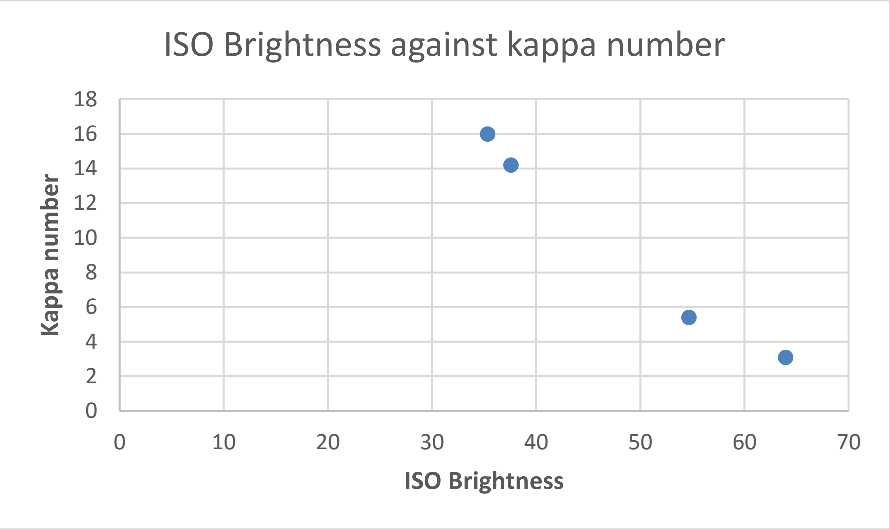

Figure 9: Kappa numbers of four pulps against their brightnesses. Pulps measured were from low to high brightness: unbleached pulp, pulp number 19, pulp number 8 and pulp number 24.

4 Discussion

Overall the bleaching reactions were successful and yielded good information, but the brightness levels remained insufficient. According to the literature, reaction parameters in this thesis were in the recommended ranges, but bleaching effect was not adequate. It might be because of the scale of our reaction which is very small against industrial applications. Differences in the scale include differences like proper mixing, air availability to pulp during reaction. This small-scale bleaching was done in plastic bags with possibilities of affecting our bleaching chemicals. Which is very different from the industrial scale and the stainless-steel bleaching tanks. Some of the differences could be tested to see if any effects can be seen. Mixing could be the easiest to try as mixing could be done continuously to a bag and similar bag could be then mixed every ten minutes to reach a conclusion.

All the graph data from the measurements is of course difficult to interpret when the measurements have been made after both reactions have been done and all the other parameters have had their effect on the pulp as well. With hypochlorite dosing having most effect the graphs are coloured to see the same dosages as a group. When looking at a group in a graph it doesn't convey the additional parameters effect at all which keeps the interpreting of the graph vague.

Oxidising reactions are sometimes used with additional oxygen fed into the reaction. Oxygen and peroxide together are known to work together as they react with different functional groups of lignin (Hart 2019). Coming back to our reaction where the reaction is happening in a closed bag where only a little air is kept and therefore very little oxygen is available. Oxygen for the reaction could be used quickly if it really is helpful in the reaction. Then again testing it would be difficult and not the most effective as trying to keep a bleaching reaction bag open and having air and not pure oxygen circulate at the pulp to air boundary.

Other bleaching test were being done with very different brightness results with similar chemical dosages with only a one-stage sodium hypochlorite reaction. Results were a lot brighter and close to ISO 85 with also DP of around 950. They were done with only one stage bleaching with only sodium hypochlorite. With the other reactions and the small batches, I believe differences could have been the mixing with more force and continuously, differences in the pulp consistency or dry content percent and availability of oxygen of air to work as an oxidiser. The differences could work to affect the end results.

Mixing of the reaction is important in the beginning of the reaction when bleaching chemical is working the most, mixing every ten minutes lets me see the bleach working in some areas but not in others as the chemical has not been mixed well enough. The areas where there is more bleach might get to a point where the bleach is using itself on pointless reactions and not to the wanted chromophore reactions, we would want it to. In areas where bleach hasn't mixed to might not bleach as other areas and might affect the brightness measurements more as there are darker fibres mixed in with the lighter fibres. In the brightness test papers I could not see this by eye as individual fibres cannot be seen and overall colour is consistent, but some fibre bundles, fibrils can be seen as darker lines in all of the papers.

Comparing the reactions of hypochlorite and the hydrogen peroxide, hypochlorite reaction seems to be much more powerful in the amount of brightening done. The amount of loss in degree of polymerisation also seems to be correlated to the amount of brightening done and not on the chemical reaction properties. More will be discussed in the next sections.

Difficulties were found setting the pH for the hydrogen peroxide reaction. The cellulose mass is a rather thick consistency and high value of dry content for the reaction. Thick consistency meant that measuring the pH from the mass was difficult as mixing the mass to achieve a stable pH all around the bleaching bag was not easy. pH value could be measured wildly different from different parts of the mass. Problem was mitigated by trying to average the pH values from several places to have an average value. Also, pH probing the mass proved to fill the pH probe measuring head. Poking the mass with the pH probe would achieve a first measurement to a clean probe, but after that measurement the probe was mostly full of the cellulose mass from the first probing spot. Therefore, the next measurement would not differ from the first. Overcoming the issue was achieved by stuffing the probe through a lot of the mass. With the aggressive probing, minimal mixing was also achieved. Probing heavily would displace enough of the cellulose mass from the probe measuring area to have new mass to measure pH from.

In hindsight, using DOE softwares to accelerate the possible optimisation of bleaching parameters was not useful in this experiment. The premiss of the usage of JMP for design of experiments was to more accurately get successive tests done in the right direction from the bleaching standpoint. But as a starting point for all the optimisation, DOE software needs to have a lot of data from a large group of tests. DOE software assessed the number of different parameters and combinations of them for one bleaching run and estimated that 25 tests would be enough for it to estimate optimal bleaching with the parameters or suggest follow-up tests after the first batch. These 25 tests used up a lot of the time of the schedule and we did not have much time for subsequent tests after the first large batch. I think DOE helps in cases where multiple parameters must be optimised and like here in multiple reactions but measurement of progress or gathering of data can only be done after all tests. In this case we also did all measurements after the tests but could see the colour changing after each reaction. So, I had an estimate of the reaction working better or worse after each reaction and could compare the colour and estimate the reaction efficiency. As we could see the colour changing from bleaching and comparing to a wanted brightness, we could always see the product being too dark or yellow to the eye to reach wanted brightness. With a measurement of DP which cannot be seen by eye it would be a different case. This experiment could also be done first with one-stage reactions and then measurements, analysis and a combination of the one-stage reactions.

4.1 What did the sodium hypochlorite reaction achieve?

Comparing the results of the first bleaching reaction after both reactions are completed may be difficult but is achievable. The first bleaching reaction still has the advantage that it could be assessed easily by eye when doing the experiment and bleaching first hand. In the moment of bleaching the dosage and the temperature seemed to help bleaching as more is more. Dosing amount seems to keep the effectiveness as more bleach is dosed to the pulp the more it bleaches.

Mixing more often or in a different way could lead to a more evenly bleached pulp. Pulp mixing has been known to be very important to an effective bleaching reaction, and with that our process could be improved. Compensating mixing difficulties could be done with reducing the dry content percentage or consistency which is the amount of dry pulp in the pulp solution. (Gellerstedt et al. 2009)

In Figure 4A, the effect of hypochlorite dosing can be seen very clearly. Adding hypochlorite in the first reaction adds brightness with other parameters making only a small difference in the bleaching reaction. All the difference other parameters make is only a small adjustment when compared to the difference hypochlorite dose makes in the brightening. Taking a trendline of all points in the graph of hypochlorite dose against brightness gets you the trendline equation which is $y = 11{,}765x + 36{,}222$. This can be used to estimate how much dosing would be enough to get our pulp to the brightness of 85 and the answer is around 4,14 %. Of course, we don't know if the effects of bleaching would keep on affecting the pulp with the same effectivity or not. Also, the trendline is considering all the other reaction parameters we used which helped in the bleaching process and hindered some bleaching reactions. Temperature of the reaction is not as important as the dosing but seems to have an effect when looking at groupings of hypochlorite dosing and more accurately the groups of 1,5 and 2 % dosing.

From the data of Table 2 we can see bags number 15 and 16 which have identical second reactions with hydrogen peroxide. Analysing them can give us a confirmed difference of reactions. Bag number 15 had a dose of 1,5 % of hypochlorite while 16 had a dose of 0,5 %. Temperatures were 20 and 30 °C respectively. Results for degree of polymerisation were 1311 and 1478 respectively and the ISO brightnesses were 51,37 and 40,52 respectively, which are large differences. The difference of brightness and DP are because of the dosing and temperature differences. From the Figure 4 graph we must deduce that most of the bleaching effect in the first reaction is from the dosage of the bleaching chemical. Temperature is not as important but still matters as temperature rise was seemingly effective at helping the bleaching process as the colour differences could be seen before the second bleaching. In the graphs, temperature effect is difficult to see after the second reaction makes its effects on the bleaching. The effect of temperature is still much less than the doses effect.

Assessing temperature effect on sodium hypochlorite reaction can be done with bag 11 and 14 which have the same hypochlorite dosing of 1,5 %, temperatures of 35 and 40 respectively. After first reaction the bag number 14 gets by my understanding more effective reaction with all parameters of hydrogen peroxide dosing 1 % against 2 % of bag 14, 40 °C against 50 °C and 11 pH against 11,5 respectively. But then comparing results of the two bleaching reactions which are similar to each other with values in DP of 1118 and 1144 respectively, with ISO brightness being 56,34 and 56,57. After the value for dosing of 1,5 % to both of the pulps, the set of parameters was harsher for the bag 14 which did not achieve much bleaching performance from the parameters as results are so even. Temperature of the hypochlorite reaction might already be optimal around 35 and 40 °C might already be over the optimal temperature or only have the same effect.

4.2 Observations about the hydrogen peroxide reaction

Dosing of the hydrogen peroxide is not a similar major factor of the reaction. It seems that the other parameters of temperature and the starting pH of the reaction have an equal effect on the bleaching activity. In the Figure 5 we can see a rising trend of dosing being beneficial in the groups of blue and yellow, which represent the sodium hypochlorite dosage of 0,5 and 1 %. The groups have a slight upward trend at highest dose of 2 % but the brightnesses of other dosages are steadily in the same line with not much brightness increase with dosage.

The group which didn’t go through sodium hypochlorite reaction could have been an easy place to compare the next reactions effects. But as the pulp in that case was totally unbleached, hydrogen peroxide in these amounts did not achieve any colour change by eye. Amounts and reactions of hydrogen peroxide could have been starker to see stronger differences. The amount of difference from the bleaching samples are a difference achieved by bleaching and not within a margin of error in the measurement stage. To have a better understanding of this reaction, many more of samples should have been completed with only the hydrogen peroxide reaction. Of course, workload would be added with that.

As the second reaction of the reaction chain is more difficult to analyse, there might be more to the hydrogen peroxide reaction than only dose. The only easily analysable samples are the unbleached group until the hydrogen peroxide reaction. The three of them, got a very varied reaction but still managed to achieve very similar values in DP and brightness measurements. The most interesting result is that the soe is not the clearly most telling parameter of this reaction. As the group got doses of 0,5; 1 and 2 % the results are that lowest dose was the brightest and highest dose was darkest. The results are very close to each other but still I believe the difference of them as the measurement is an average over six measurement spots. This hydrogen peroxide reaction might have a very balanced load on every parameter of the reaction as the brightest paper did the smallest dose but highest temperature of 80 °C and high pH of 11. Second highest brightness had the dose of 1 %, temperature was only 50 °C, but then pH was the highest 11,5. Darkest pulp had the largest dose of 2 %, low temperature of 60 °C and low pH of 10. Therefore, the bleaching reactions effects could be very similar as the reactions are very different but all of them have an edge over the others in one parameter. Comparing to the sodium hypochlorite reaction where dose was the key to success, these three the results make the reaction parameters equally important. The optimal parameters for bleaching in the second reaction of hydrogen peroxide should be the strongest here and maybe more on dosing. At least the reactions should be tested to the dosing of 2 to 5 % where pH would always be 11,5 and temperature 80 °C.

Comparison of reactions number 22 and 25 can also allow us to separate the action of sodium hypochlorite from the second hydrogen peroxide reaction. Bags 22 and 25 had the same reaction in the first round of bleaching with the hypochlorite reaction conditions of 0,5 % dosing and a low 20 °C. Differences in the hydrogen peroxide reaction is dosing of 0,5 % against 1 %, temperature of 40 against 80 °C and pH of 11,5 against 10 respectively. The bag number 22 with lower dose and lower temperature with a pH of 11,5 achieved better results in brightness. Again, the differences are miniscule but telling. Comparing the brightnesses which are 40,89 and 40,74 respectively. Reaction number 22 has a disadvantage in both the dosing and the temperature but still manages to bleach pulp stronger than number 25 is valuable information. The pH value is very important to be high to be an effective reaction. Surely high dosing and temperatures would help too but the significance of pH should not be underestimated.

With the comparison of tests 9 and 13 I think we can see the pattern of the hydrogen peroxide reactions. Bag number 13 had mildly, if at all, weaker hypochlorite reaction with only the temperature change of 35 to 40 °C on bag 9. Hypochlorite reaction being with similar results or weaker, the bag number 13 could in the hydrogen peroxide reaction get an ISO brightness difference of 2,85, which is quite substantial for the peroxide reaction. Differences between bags number 9 and 13 were the dosing at 1,5 and 2 %, temperatures at 40 and 70 °C and pH at 10 and 11,5 respectively. Bag 13 had all parameters better than bag number 9 and the difference achieved was significant.

4.3 Washing could affect the outcome of bleaching

This washing does not remove all already broken-down lignin from the pulp, which could be seen after bleaching when freeze-drying. As freeze-dried cellulose is soft and fluffy, lignin is left as a darker and different looking material on top of cellulose in the freeze-drying process. This kind of washing might remove some broken-down lignin but could also remove some smaller cellulose which might have broken in the reaction. If filtration of smaller cellulose monomers happens, amounts should be low but would affect the measurement of cellulose degree of polymerisation. Tests about the runoff from washing should be done to confirm or deny. By washing same pulp separately for different amounts, would work for this.

4.4 ISO Brightness measurement and degree of polymerisation

In Figure 8, the correlation of brightness and the degree of polymerisation of cellulose is most certain. Brightness is achieved by reactions which also affect cellulose polymerisation. We can also see that the coloured groups in the figure are usually in a different trendline. The solid trendline of the whole bleaching reactions is steeper than the dotted lines of each grouping. As the groups are differentiated by the hypochlorite dosing and each group has a gentler sloping trendline, the hypochlorite dosing is the strong differentiator which makes most of the steepness. From the formula $y = -0{,}0469x + 109{,}72$ of the main trendline we can calculate the point which could be achieved if correlation of these values stays the same. When brightness value would get to 85 the degree of polymerisation of cellulose would be 527,08 if the amount of bleaching would correlate with the amount of brightness outside the test parameters.

In literature the amount of bleach used and the amount of brightening happening in a single reaction is known to be a curve which stables off somewhat (Bajpai 2018; Hart 2019; Sapuan, Ainun, Zakiah, ja muut 2023; Suess 2010). Using more and more chemical will help less and less bleaching. Our graph is not showing signs of that happening, but our doses were quite small and close to each other.

Comparing the two reactions together might have shown that the hypochlorite reaction would achieve a steeper trendline in Figure 8. The steeper trendline of hypochlorite would mean that the hypochlorite would be more effective only reacting with lignin and not damaging cellulose as much as peroxide. Comparing bags number 9 and 13 which have the same DP in the results but a little different brightnesses of 40,59 and 43,44 respectively. They had gone through very similar hypochlorite reactions of 0,5 % dosage and 40 and 35 °C temperatures respectively, where the 40 °C reaction should be stronger but maybe only slightly. Peroxide reactions continued with a milder reaction to bag number 9 with 1,5 % dose at a low 40 °C and pH of probably too low 10,5. Bag number 13 had a stronger reaction which had a 2 % dose with 70 °C and pH of 11,5. These reactions achieved very different brightnesses with same DP in the end. Bag number 9 had slightly stronger hypochlorite reaction and lost DP in that a little more for similar or bit better brightness. Then in the second reaction which was stronger for bag 13 but at the same time it probably had better pH and temperature for peroxide to react with lignin only saving DP while bleaching. Separating the effects of individual reaction parameters from peroxide reaction is difficult when both reactions were done together.

4.5 Observations from alpha-cellulose measurements

Concluding the alpha-cellulose measurement, the values of amount of alpha-cellulose in the end sample were over 100 % but are comparable to each other. Low dosing of both sodium hypochlorite and hydrogen peroxide with low temperatures seem to be the key to retaining alpha-cellulose. pH might not be a valuable parameter when thinking about alpha-cellulose but in this small sample size of four it is difficult to conclude effects. When doing bleaching reactions with more extreme dosing and temperatures, then alpha-cellulose amount could be in concern, but with these parameters, alpha-cellulose amounts stayed very good.

Bleaching reactions could have been done separately to ease the analysis of reactions. It would result in many more measurements in of DP, brightness, kappa and alpha-cellulose, but analysis of the measurements would be very easy to compare to each other. After finding most effective reactions separately, the bleaching reactions could have been combined to evaluate the reactions together.

4.6 Kappa number measurements

Kappa number didn’t reveal anything new about the bleaching reactions. Kappa number was expected to be negatively correlated with ISO brightness as it was. Interesting and maybe obvious with the foresight is that the ISO brightness rises very slowly as kappa number drops in the lower effectivity reactions but in with the higher effectivity reactions a small improvement and lowering of kappa number is a larger jump in brightness. The more you achieve bleaching, the more effective lignin removal is to reach higher brightnesses. In the brighter stages of the bleaching every lignin amount removed is easier to see as brightening than in the darker stages of bleaching. The last lignin should also be the most difficult to remove with keeping the cellulose degree of polymerisation intact. Continuing the experiment, the measurement of kappa is not a worthy measurement as it does not carry much additional information with it.

5 Conclusions

Efficient bleaching reaction workflow was achieved, and the bleaching reactions went successfully, but not without problems. Measurements of degree of polymerisation and ISO brightness went well and yielded good correlating results. Additional measurements of alpha cellulose and kappa number were done to see to confirm measurements.

Bleaching with sodium hypochlorite and hydrogen peroxide were done successfully, and sodium hypochlorite was proven to be more effective at bleaching without additional damaging effects on cellulose degree of polymerisation. Hydrogen peroxide reactions more elaborate parameters and measuring them troubled us but after this experiment package we found better reaction parameters to use in the future. Sodium hypochlorite was effective but the dosing from 0,5 to 2 w-% proved to achieve too little in our bleaching system for our raw material of oat husk and the target of ISO brightness 85. Temperatures for the reaction should be 35 to 40 °C in the small-scale bleaching reactions and higher temperatures should be tested. Remarks from outside our reaction parameters is that the sodium hypochlorite reaction needs strong mixing in the beginning of the reaction, which is maybe difficult to achieve in small-scale bag bleaching.

Hydrogen peroxide bleaching was less effective than hydrogen peroxide at our dosing of 0,5 to 2 %. The bleach dosing was less relevant to the effectivity of the bleaching than in sodium hypochlorite reaction. With the right temperature and pH, bleaching could achieve brighter results with lower amounts of bleach. The temperature for the reaction should be high from 70 to 80 °C but maybe even hotter. pH for the reaction is important and should be from 11 to 11,5 or higher in the start of the reaction.

To enhance bleaching effectiveness, reaction parameter values should be expanded up for almost all parameters as degree of polymerisation was still high at over 900 for all reactions. Degree of polymerisation drop from the bleaching reactions was not as severe as thought beforehand. For sodium hypochlorite dosing can be raised at least to 4-6 % which should still achieve cellulose in good enough condition for food and cosmetics use. Temperature of sodium hypochlorite reaction can be optimal in 35 to 40 °C but higher temperatures should be tested. Hydrogen peroxide was much less effective and the use of it should be considered. If used, hydrogen peroxide dosing should be raised from 2 % until it gives effective results. The other parameters were effective at high temperature of 70 to 80 °C and pH of 11,5 or higher. Outside our original experiment plan, the pulp viscosity or consistency will affect the mixing effectivity as less dense pulp is easier to mix. The bleaching chemical is difficult to get everywhere if pulp consistency is high. For hydrogen peroxide reaction and maybe sodium hydroxide also, oxygen may help the bleaching reaction and availability of oxygen in the reaction bag should be tested. Bagged reactions in our experiment had little to no air and therefore oxygen in them. Washing the pulp more might also affect the brightness of pulp but was not experimented with in this work.

Experimentation continues at CH-Bioforce to allow us to achieve a bright white cellulose product for the food and cosmetics industries.

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Appendices