

Lappeenranta-Lahti University of Technology LUT

School of Energy Systems

Programme of Energy Technology

Master's Thesis

Usability of digester screens in dissolving pulp production

Keittimen sihtien käyttövarmuus liukosellun tuotannossa

Examiners: Esa Vakkilainen

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Lappeenranta 27.9.2021

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ABSTRACT

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Examiners: Professor Esa Vakkilainen and D. Sc. (Tech.) Katja Kuparinen

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The target of thesis is to study an existing issue of digester surface scaling in dissolving pulp production. Capacity of dissolving pulp production is increasing globally every year and resolving typical issues that the process faces can benefit several mills across the world. Future of the viscose will focus more on wood-based production as technologies of dissolving manufacturing will become more efficient and variety of end-products will increase.

During dissolving pulp manufacturing process scaling accumulated on the process surfaces can cause significant process issues. Based on related literature it can be said that in the digester vessel and blow tank have varying conditions in terms of alkaline and pH which would indicate that calcium carbonate is present and primarily causing the issues. Based on real life cases and existing studies in current situation of scaling is studied and theory behind can be explained. Ways to remove that scaling from surfaces without production losses are also studied. It is obvious that to reach the best possible outcome a combination of several methods, such as process control and chemical extraction, and

vast process knowledge, instead of singular actions is best method to resolve issues in mill level. Especially in prevention of scaling can be highly cost-efficient method.

TIIVISTELMÄ

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Tämän diplomityön tavoitteena on tutkia liukosellun tuotannossa esiintyvää prosessipintojen saostumista. Liukosellun tuotantokapasiteetti kasvaa vuosittain maailmassa ja tyypillisten prosessiongelmien ratkaisu voi hyödyttää useita tehtaita ympäri maailman. Liukosellun tuotanto tulee jatkossa painottumaan enemmän puupohjaiseen sellun tuotantoon kysynnän kasvaessa, ja tuotantoprosessin tehokkuusparannukset sekä potentiaalisten lopputuotteiden määrä tulee kasvamaan.

Tuotettaessa liukosellua prosessipinnoille kerääntyvä saostuma voi aiheuttaa merkittäviä ajettavuusongelmia tehtaalle. Kirjallisuuteen pohjautuen voidaan sanoa, että keittimen ja puskutankin alkalisissa ja vaihtelevissa pH-olosuhteissa saostuma on tyypillisesti pääosin kalsiumkarbonaattia. Tosielämän tapauksiin sekä nykyiseen tutkimustietoon pohjautuen erityisesti keittimen sihtien pinnalle syntyvää saostumista tutkitaan sekä sen teoriaa käydään läpi. Etsitään myös mahdollisuuksia poistaa saostumat ilman tuotannonmenetyksiä. On selvää, että parhaaseen mahdolliseen lopputulokseen pääseminen vaatii prosessin kokonaisvaltaista hallintaa ja ehkäisymetodien yhdistäminen

sekä vaiheiden tunteminen antavat keinot minimoida ongelmia. Erityisesti ennaltaehkäisyyn panostamalla voidaan saostumisen riskiä pienentää taloudellisesti.

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LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviations

AC	Acid sulphite
BC	Batch cooking
CS ₂	Carbon disulphite
CC	Continuous cooking
CCE	Cold caustic extraction
DP	Degree of polymerization
ECF	Elemental chlorine free
HCE	Hot caustic extraction
MWD	Molecular weight distribution
OXE	Oxidizing equivalent
PHK	Pre-hydrolysis kraft
PHL	Pre-hydrolysis liquor
TCF	Total chlorine free
VA	Violuric Acid

1 INTRODUCTION

Dissolving pulp is a wood-based material primarily used on textiles production, namely viscose and its subvariants. Over 60 % of global textile production was based on fossil-based synthetic materials in 2016. That means annual textile production of over 79 million tonnes was based on fossil-based raw material, growing by 60 % in 10 years period. During this same period, natural fibres showed growth of only 2 million tonnes, or 9,2 %, most of this being cotton, accounting 27 % of global textile raw material. (Krifa & Stevens, 2016)

In the upcoming years, it has been estimated that need for textile raw material will increase faster than new cotton production areas can be implemented. Cotton also takes up land area that could be used for food production. Cotton also requires stable atmosphere and constant amount of watering over the growth season. This market gap between ability of implementing cotton fields and increasing demand for textile creates a potential demand for high volume textile raw material production, with lesser impact on environment compared to fossil-based synthetic materials, with steady availability and price. This is where dissolving pulp can help.

Dissolving pulp is typically wood based pulp with high cellulose content of over 90 %, with less hemicellulose than in paper-grade pulp production, typically ranging between 3-6 %. Due to high refining level, also contents of lignin and other impurities are lower than in regular paper-grade pulp. Dissolving pulp production is large and every year increasing sector of pulp production industry on global level. Around 90 % of all dissolving pulp is made from traditional pulp materials, softwood or hardwood, and 10% out of cotton linter due to high price and selected end-applications with higher purity requirements. (Sixta et al., 2013).

Generally, end-products of dissolving pulp can be separated into four main categories, regenerated cellulose, cellulose esters, cellulose ethers, and other products, such as Nano and Micro celluloses. Different end-uses require different qualities from pulp material and field of end-uses is vast with several specialized products. More and more end-uses are being created every year. The most common end-use is viscose, requiring the lowest purity of different varieties within the category of dissolving pulps, and it is used for textiles

production. Second most abundant use of dissolved cellulose in terms of annual production volume is cellophane, discussed in following chapters and cellulose acetate, part of cellulose esters, which is used for membranes, films, coatings, and various other end-uses. (Sixta, 2013) According to its name, cellulose acetate is produced with substituting hydroxyl groups of cellulose with acetyl groups, affecting water solubility and viscosity. (Watabe, 2018) When talking about pulp production process, all dissolving pulps are manufactured with cellulose raw material, and variation depending of the end-use begins only after removal of lignin, hemicelluloses, and other impurities.

The main topic of the thesis is related to digester and pre-hydrolysis vessel of dissolving pulp mill. Both vessels have screens, like in ordinary pulp production, but especially in the dissolving pulp production there have been mill cases that the screen slots can get plugged due to scaling. Plugging of the screens causes variety of difficulties for mill process and production wise. Most notable issues caused by plugged screens is that liquor cannot be extracted from digester properly through plugged slots of the screens in proper manner. On general level, availability of screens and effective area have a major impact on energy and process balances within mill and directly affects cooking result out of the digester.

Direct consequences are seen in pumping with lower black liquor flow, imbalance in heat and chemical recovery from black liquor due black liquor not getting into circulation and potentially insufficient impregnation on the top of the digester followed by poor quality of cooked pulp after digester. Indirect consequences include higher load on further fiberline on bleaching and drying equipment due to lower or at least suboptimal consistency going into blow tank, leading to higher bleaching chemical consumption, and potentially weakening pulp quality, impacting negatively on price of pulp or even by lowering cooking capacity. All these points directly affect energy, economic and chemical consumption of the mill, directly or indirectly affecting the safety and controllability of mill functions.

1.1 Scope and outline of work

This master's thesis focuses on usability (or availability) of digester screens on dissolving pulp production. Known issue in dissolving pulp production, especially in continuous

cooking, is that due to several reasons discussed in this thesis, scaling of digester screens in process surfaces occurs. In theoretical part, the process of dissolving pulp is explained, most common theories are discussed and the potential reasons for scaling are studied based on literature. In practical part the test run is explained due to test runs could not be completed in time. The target of the practical study would be to resolve if these coating actions can help with issues scaling causes and if it would be profitable for the mills with scaling issues to launch coating actions and apply the coating for the digester and pre-hydrolysis in the large, mill size scale.

Theories on how this scaling can be affected or reduced are discussed, including which chemicals can affect the scaling on fiberline, to control of temperature and pH value of digester environment can affect the scaling and how mills currently react or what precautions are done in order to resist the influence of scaling in the fiberline. Methods of screen coating are explained, and best potential practises are briefly presented.

As one of the drivers for development of the coating method of digester screens is commercially viable product, so in the end a brief economic evaluation is performed to find out of use of coating for the screens is economically viable. To evaluate this economic aspect, return-of-investment time is calculated in comparison to how scaling in treated normally during maintenance shut down and potential what kind of work is needed to remove this scaling.

The scope of the work in theory part is to first go through most common commercial processes in wood-based dissolving pulp production, compare the dissolving pulp production to paper-grade pulp production, study of the current trends of dissolving pulp and why the production has increased steadily over the last few years. Some of the basic chemistry in dissolving pulp production is also discussed and most important compounds are noted. Second part discusses the chemistry of related issues that cause the scaling, and tries to resolve the possibilities of coating the screens in pulp mills. In the end discussion is done if these methods are economically viable in comparison with alternative maintenance methods for scaling issues.

Scope of this work is limited so that it focuses on wood-based dissolving pulp production, which means cotton linters and its cooking processes in details is excluded, while still noticing where and which applications cotton linter-based dissolving pulp is used. This is important because most of commercial applications suffering from scaling are wood based applications and greater amount of global production is based on wood, which this thesis work will attempt to solve or at least discuss new method of reacting and help pre-treat the issue. Applying these study results for cotton linter process could be a topic of further study, if any scaling in similar manner within cotton linter production occurs.

Process-wise this thesis only focuses on process starting from chipped wood and ending to commercial dissolving pulp, not accounting its end-production processes and refining the pulp to viscose or other possible end-products, other than in brief history chapter which gives basic concept of wood-based dissolving pulp production and future trends, as xanthation process is one of the key issues deriving social and environmental issues within viscose production today.

This thesis focuses on technical and economical side of dissolving pulp and scaling issues, but it also touches environmental aspect of dissolving pulp in general level, classifying things in order by more environmentally friendly versus less environmentally processes and production. However, these aspects are done only to provide additional information, and not to study the dissolving pulp production's environmental aspect, although this could be interesting topic for future studies. This thesis also focuses on explaining theories of continuous digesters, however it should be possible to apply these same methods to batch cooking equipment, as far as process values are considered. Some studies have empirically noticed that less batch digesters suffer from the scaling in comparison to continuous digesters. Some notes in theory chapter is made on batch cooking equipment, as they are also in major role in potential conversion mills, as many smaller batch digester mills are producing paper-grade pulp, with large demand drop in last years. It could be one of trends that paper-grade producing batch mills could convert into dissolving grade production.

2 DISSOLVING PULP PRODUCTION AND INDUSTRY OVERVIEW

Global dissolving pulp capacity is little less than 10 % of the global market pulp, capacity being around 9.5 million tonnes and production of 7.07 million tonnes. Biggest importer and consumer of dissolving pulp is China, consuming up to 4.9 million tonnes or around 69 % of global dissolving pulp to their production. (Young, 2017)

Biggest producer of dissolving pulp is also China with its production of 1.9 million tonnes in 2017. Together with North and South America, China account over 50 % of global production of dissolving pulp. Production of dissolving pulp has grown rapidly over the last 15 years, with new mills in China increasing their own dissolving-grade production and some major global companies piloting on either new mill on industrial level or converting existing mills to flex lines, with potential producing both paper-grade and dissolving pulp. (Young, 2017)

Fastest growth period in 2010-2013 in dissolving pulp production was due to high prices of cotton over that period. Even within Europe a quick spur of mills converting into dissolving pulp has happened, doubling within last 10 years. Especially notable trend has been former paper mills struggling against falling global consumption converting into producing dissolving pulp to steadily growing market. In addition to China, other countries with notable dissolving pulp production sites (mills) are the United States of America, South Africa, Canada, Austria, Sweden and Brazil. (Young, 2017)

Areal differences of quality of produced dissolving pulp also occurs. In general, most of lower purity production viscose is done in China, while higher purity applications are protected by patented production processes in integrated mills and smaller companies around the world. These higher purity applications have specialized markets which makes them separate from major dissolving pulp business, where as China is focused on high volumes of commercially cheaper and technically simpler viscose production to support their textile industry. (Viitala, 2016)

When discussing about the advanced applications for example, Lyocell process used and owned by Austrian Lenzing AG, has different attributes in the means of higher strength and

it is produced with different method when compared to traditional dissolving pulp-based viscose. Another variant from traditional bulk market is Norwegian Borregaard company producing variety of products of highly refined pulp-based products, 2nd generation bio ethanol and their LignoTech lignin-based products. (Viitala, 2016)

2.1 History of dissolving pulp

History of cellulose fibres usage is quite vast, but the concept of cellulose-based textiles that could be considered the beginning of viscose generation, was first discussed in 17th century by Robert Hooke. He wrote in 1655 that it would be possible to imitate silkworm's silk by artificial glutinous composition. Cellulose was still discovered only in 1839 by Anselme Payen, almost 185 years after Hooke's concept. However, production of derivatives of pure cellulose was first successfully implemented in 19th century in form of cellulose nitrate by George Audemars. Before this, Louis Schwabe had invented the concept of spinneret with that could be implemented for production of fabrics for cellulose. (Woodings, 2001)

High price of silk was still a driving factor for development of artificial silk fibres all the way to the late 19th century, when first commercial process of production of denitrated cellulose nitrate from treated mulberry tree leaves by Hilaire de Chardonnet. Treatment of the leaves was done with nitric and sulphuric acid and dissolved with ether and alcohol. The process of chemical treatment with several chemical phases during time when chemicals weren't widely available, was slow, not very scalable to mass production and uneconomic, but it gave a commercial base for artificial fabrics production. Process was in commercial use all the way until 1949, although alternative cellulose fibre production processes had been developed parallel with Chardonnet's invention. (Woodings, 2001)

Viscose Rayon production theory via xanthation and alkali and CS_2 treatment was discovered in 1891 and patented in 1892 by Charles Cross, Edward Bevan and Clayton Beadle. This process is currently most used Rayon production process. They used ammonium sulphate as coagulation agent and dilute sulphuric acid for bleaching. Early licenses at the time were related to other side products than developing viscose Rayon for textiles but used more for example in paper industry as coating, rather than its own product.

Commercial spinning of viscose from wood-based material was capitalized by Charles Stearn after realization of viscose process and contacting Charles Cross. Although the process existed and remarkable technologies related to viscose process had been developed, the first successful spinning plant for rayon yarn did not exist until patented by 1904 in Donnersmarck with Müller's SpinBath technology. (Woodings, 2001)

Major development in SpinBath technology in 1907-1911 was seen after commercialization of the process, such as addition of glucose, patented in 1907, extraction of ammonium salt in 1909 and zinc sulphate addition in 1911, improving acceptable yield according to standards set at the time. Still yarn produced by Viscose process was only about one sixth of all artificial fibre yarn in terms of production volume, whereas half of all artificial fibres was produced with nitrate process and one third with cuprammonium process. (Woodings, 2001)

After expiration of viscose process patent in 1920, artificial fibre market increased significantly, and after basic chemical process existed and commercial process could be applied, new developments were focused on increasing the strength of yarns, and new end-uses were developed such as tyre-yarn, supporting new car market after (or in between of) war period. In 1941 first synthetic polymers were discovered, booming the market with Nylon and polyester and replacing the viscose rayon as biggest artificial textile source and forcing the development of viscose process to keep it competitive, not necessarily on textiles sector, but many alternative ones. This ended the initial straight-line development of dissolving pulp that had started in late 19th century as dissolving pulp serving only one product and dissolving cellulose producers started specializing in several, smaller sectors and end-uses as textile market became economically unattractive. (Woodings, 2001)

Good example of company based on viscose process production was Samuel Courtaulds & Co Ltd. Being a major player in artificial fibre market since development of SpinBath, new company strategy was implemented when synthetic polymers were taking over, including partly converting out of viscose and using acrylic fibres (also synthetic polymer) with wet-spinning and developing new products like acetate-based products as well as adding value to their own refining chain with new products, even by company acquisitions. (Woodings, 2001) All in all, commercialization of synthetic polymers meant diminishing market for

regenerated cellulose fibres with older technologies with highly available oil refining and moderate oil (raw material) price.

Much later, same company was heavily involved with commercialization and developing of Lyocell process, even today being commercially implemented by Lenzing AG. (Woodings, 2001) As seen on last years, increasing production of viscose is returning to textile markets but the growth rate is still not replacing nylon and polyester base fibers, but only filling the gap with high-cost cotton.

2.2 Growth of dissolving pulp capacity

Continuous additions for global capacity of dissolving pulp are driven by few factors. Primarily, new installations are producing dissolving pulp raw material for viscose rayon production, which is an alternative for cotton and fossil-based textiles which are primarily found in market these days. Reasons for popularity of this new technique can be split into environmental, economic, and social reasons. It is also worth mentioning that increase of global dissolving pulp production is thanks to the growing markets of China and India consuming large portion of annual dissolving pulp production.

Environmentally, first reason for growth for dissolving pulp production is the high availability of raw material globally, either softwood or hardwood can be used, depending on the process. Second strong driver is that cotton, unlike wood based raw material, competes with land areas used for food-production as discussed already in the introduction. Cotton also needs vast amounts of water, fertilization, and weeding, whereas wood-based materials are mostly self-sufficient in proper environment. Environmentally aware consumers prioritize these fibres over synthetic fibres, and possibly also over cotton, if the whole production line from wood to fibre is sustainable, and this trend will further strengthen in the future.

Economic reasons for increasing production are related to altering price of raw materials due to variation of annual production and harvest of cotton, structure, and layout of paper-grade mills, such as chemical usage and availability and conversion of current production lines to dissolving pulp. In early 2010's price of cotton fluctuated strongly. Especially the dissolving

pulp had gained the popularity in China over the last few years because the subsidies for cotton production pushed base prices of domestic cotton to lower than viscose staple fibre around 2014. (Young, 2016) High availability and relatively stable price of woody raw material has driven some producers to start dissolving pulp production. More recent trends show that some mills have also been converted to produce dissolving pulp from previous paper-grade chemical pulp, as it is possible to produce both paper and dissolving pulp on same mill within the same fiberline. This will be further concentrated on later chapters.

Social reasons are strongly related to environmental reasons, since areas and people producing cotton, are strongly dependent of the income that cotton provides them. Even though cotton production requires more attention in form of fertilizing and watering, its growth cycle is much shorter compared to woody resource, even when compared to tropical, quick growing wood species. Notable is also higher yield per land area for cotton when comparing to wood raw material. These issues might make it difficult to transit from cotton-based raw material to wood-based material on local level without subsidies and assistance. Cotton farms also rotate cereal crops, such as maize and wheat, to minimize risks of diseases and pests, which is difficult with wood-based materials and these local food-production crops provide safety for the farmers and local communities. However, cotton is more susceptible to weather conditions, so transition to wood-based raw material growing which might bring safety to farmers on longer time frame.

3 MODERN TRENDS OF DISSOLVING PULP

Dissolving pulp production serves completely another customer sector than traditional paper-grade pulp production. Traditional paper-grade pulp is typically used to produce paper or board within the same mill area or sent to separate board mill, whereas end-users of dissolving pulp mills are not integrated and not using the pulp themselves, however, exceptions do exist. The most typical dissolving pulp end-use is regenerated cellulose, used in textiles production viscose fibres, commercially named Rayon, as referred in the history chapter, with other end uses being cellophane, used in packaging and wrappings. In the figure 1 is a breakdown of most common different applications of dissolving pulps and end products.

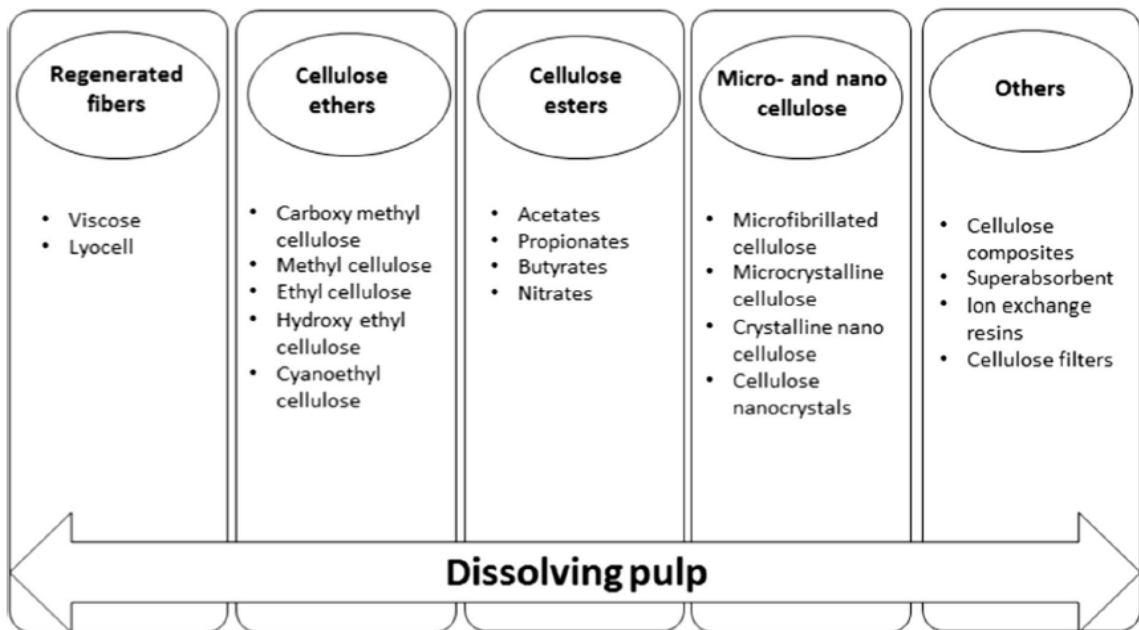


Figure 1. Refining and major end uses of dissolving pulp variants (Kumar, 2017)

3.1 Correlation between price, refining and purity

Even if degradation of cellulose within the cooking process would be completely nullified, yield of higher purity cellulose from wood-based application even in theory is lower, because of the natural content of cellulose is low in woody raw material. This means if hemicelluloses cannot be refined to high-quality cellulose, cotton linters will stay as prioritized raw material

for higher purity products. General content levels of cellulose of both hardwood and softwood can be seen in the figure 2. In addition, hardwood typically have higher extractives content (2-8 %) than softwood (1-5 %).

	Content [%] Softwoods	Compound Hardwoods
Cellulose	40...44	40...44
Hemicelluloses	30...32	15...35
Lignin	25...32	18...25

Figure 2. General content levels of substances in typical woods (Sixta, 2006)

In general, it can be said the higher the degree of purity of dissolving pulp, the more processing it requires and the more expensive the purification process of the pulp from chips to pulp is. Noting that required purity should be found out before designing the process. Later equipment additions to capital investments can cost a lot in comparison to main project where the whole process is considered.

As discussed above, when talking about end uses, wood-based pulps are used for regenerated cellulose used for viscose rayon and Cellophane production. With better refining processes it is also possible to get higher purity cellulose with enough alpha-cellulose content for higher purity uses but yield will suffer. However, applications of cotton linter-based pulp are most of the time used in higher purity derivatives of cellulose esters, such as cellulose nitrate and cellulose acetate and ethers with higher viscosity, like methylcellulose due to higher market price and much easier refining from already high alpha-cellulose content in comparison to wood-based material.

3.2 Current trends of dissolving pulp production

Dissolving pulp market is dominated by viscose Rayon producers, as it could be argued to be more attractive material to consumers than those made directly with fossil-resources

based fabrics or water-intensive cotton with generally accessible prices. Dissolving pulp doesn't suffer from fluctuating prices based on harvested raw material as much as regular cotton and the chemical costs can be considered to be on fairly stable price levels overall. Areal annual variation can impact price due to the destroyed yield by increased areal prices and weather phenomenons can impact the harvest season therefore impacting the prices. Most important trend globally is that the amount of regenerated cellulose used for rayon production has also increased much faster than specialized, very high-alpha pulp production, such as acetates, esters or cotton linter-based production.

Newer applications including micro- and nano-crystalline celluloses with various end uses in food and cosmetic industry are showing slow but steady growth. (Sixta, 2013) Market share of the other products is relatively small and growing smaller, but this is rather thanks to high increase low-alpha dissolving pulp growing extremely high rate. New applications of dissolving pulp are being studied and developed all the time, namely nanocomposites and 3D printing application. As the development of these newer applications reaches higher availability, it's popularity and volumes will grow, lowering its unit costs and making it more and more attractive for new end uses. It is also likely that at some point cotton linter-based production will be replaced with wood-based, but with current technologies the use of cotton linter for high-alpha products is more economic due to high refining prices.

3.3 Drivers of change

When talking about modern trends of any major industry sector, it can safely be said that trend in the increasing volumes are related to environmental themes and increasing economic potential. Production and end-uses for dissolving pulp are no different in this light. Dissolving pulp production has been developed to be more environmentally friendly by developing new methods to extract hemicelluloses softer and more effectively, using mechanical and chemical treatments for improving reactivity, minimize use of bleaching chemicals and chemicals altogether.

Other drivers have been mainly economic and output improvements. To name some, change to using fast growing wood and non-wood species where the production is specialized on

commercial wood, which increase the local availability of raw material, extraction of side-products from cooking and (PHL) liquor, to gain additional value for mill and IONCELL process for separation of high-purity hemicelluloses with ionic, selective liquid. (Kumar, 2017) IONCELL process also recycles the separation chemicals within the extraction process. Some of the most remarkable technologies are discussed in Kraft process chapter where most of these technologies are implemented mostly in Kraft process.

Some setbacks are also related to these new improvements. Increase in fast growing wood and non-wood raw materials, such as fast-growing wood species, jute sticks and corn stalks can require changes in cooking methods due to different (typically lower) lignin and hemicelluloses content, resulting in issues related to extraction of these from pre-hydrolysis liquor and lignin recovery. (Kumar, 2017) This could be done with selective substance removal as alkali and enzymatic treatment, but this is also affected by low organic content in pre-hydrolysis liquor.

3.4 On-going projects

There are several upcoming projects that are focusing on the treatment of pulps to produce textile raw material even in Finland and manufacturing raw material from various sources. Spinnova uses purely mechanical process to produce MCC from several raw materials, Metsä Group is developing its process and targeting 50 000 tonnes of annual textile fiber production from wood-based materials. Infinited Fibre is planning to produce new textile raw material from recycled clothes and other cellulose-based material with carbamation and wet spinning. IONCELL process is being developed to produce dissolving pulp directly from kraft-pulp. (Ikävalko, 2021) Two key trend of the development projects are to reduce or completely get rid of CS₂ used in xanthation processes, as well as lowering water and energy consumption of the process.

4 DISSOLVING PULP PRODUCTION

The two main commercial production processes to produce dissolving pulp from wood raw material are pre-hydrolysis kraft (PHK) and acid sulphite (or sulfite) (AS) processes, of which 56 % of worlds dissolving pulp was made with PHK and 42% with AS process. Out of all dissolving pulp globally, around 83% was used for viscose production. (Sixta et al., 2013) After 2013, most of the added capacity is also viscose-based production. In early 2000's most of dissolving pulp capacity was based on AS process. (Sixta, 2003) New installed base for dissolving pulp has been very rapid and most of it has been based on PHK process. This shows a trend of increase in PHK process popularity and slow transfer from softwood to hardwood, for which PHK can be more easily applied to.

4.1 Wood yard and chip preparation

Wood is brought to pulp mill as whole trunks from forest or dedicated plantation. It is beneficial to gather wood as close as possible from mill, and transport them as debranched via ships, trucks, or trains, to minimize the transportation costs. Primarily, wood should be processed (converted into pulp) as fresh as possible which limits the storing time of the trunks and especially wood chips. Trunks are debarked on debarking phase (debarking drum) and in case mill is located on cold region, de-icing is needed during winter with steam or water. This water is also used to remove dirt from trunks arriving to barking, as the process is closed, and all the additional substances affect the quality of product. Removal of bark is essential because it affects the strength properties and brightness of pulp. (KnowPulp, 2019)

Chip size has a major impact on pulping of wood. Too large chips cause issues with penetration during cooking and lengthens the needed cooking time or impregnation time, whereas too small chips have shorter fibre length and insufficient strength qualities. Modern chippers produce highly uniform chips, but screening is still performed ensure uniform product and avoid quality variation. Too large particles can be re-chipped, but too small fraction is separated and not used for pulp production. Small particles can be used for energy production on mill on traditional biomass boiler burning. Intermediate storages for wood chips can be piles on woodyard or silos before they are fed to cooking via chip bin. (Knowpulp, 2019)

4.1.1 Use of bamboo instead of wood-based raw material

In dissolving pulp production, mechanical fibre crushing (refining) is done especially for bamboo raw material and treated with enzyme for selective hemicelluloses removal. This is due to complex cell wall structure of bamboo, as it needs more pre-treatment in comparison to traditional wood-based raw materials, although its chemical composition otherwise is in between hard wood and soft wood compositions. (Chen, 2016) It must be said that dissolving pulp production from bamboo in global scale is very low, around 5 % annually. Some projects have been executed successfully in China. (Biermann, 2018)

4.2 Chip feed systems

When the chips are fed into the cooking system, chips are fed into chip bin through air lock to prevent further air entering the chip feeding system. Chip bin can have steaming feed to pre-treat the chip to remove air from within chips. Steaming can also locate in separate vessel (steaming vessel) below chip bin. From the chip bin chips fall into a chip meter or to the steaming vessel. In smaller installations chip meter can be rotor-type and in the bigger and modern systems twin chip metering screw is used. The chip metering system, according to its name, controls the amount of chips fed into the cooking over time. Digester blowing can also be used to adjust the real production speed. (KnowPulp, 2011)

4.2.1 Conventional chip feeding

After chip metering, low pressure feeder is used to which increases the pressure of chips and works as a pressure lock between chip bin and pre-steaming vessel, that works in little higher than atmospheric pressure, typically around 1,2-1,5 bars. Conventional chip feeding system typically has separate pre-steaming vessel, especially if there is no pre-steaming option in chip bin. Pre-steaming vessel is also screw feed-based system, like chip metering screw. In conventional system pre-steaming is followed by chip chute where liquor is mixed to chips, after which the chips are fed into digester pressure via high-pressure feeder. Chute circulation liquor is used to impregnate chip within high-pressure feeder. Extra liquor is extracted from the bottom of feeder and feeding to further cooking is done in 10-15 pressure. (Knowpulp, 2019)

4.2.2 **Lo-level system**

Instead of low-pressure feeder and pre-steaming vessel, in Lo-level system, chips are pre-steamed within the chip bin and fed to the first chip pump through chip tube where chips are introduced to cooking liquor. From chip pump chip and liquor mixture is pumped directly into the high-pressure feeder, so no low-pressure feeder is needed. Also, chip tube is located prior to chip pump, whereas in conventional system chip chute is located after the low-pressure feeder. (Knowpulp, 2019)

4.2.3 **Chute circulation**

In conventional and Lo-level systems, most of the circulation liquor is fed into the chip flow via chip tube or chute and extracted via bottom grid of high-pressure feeder. Chute circulation includes equipment to extract impurities from chute circulation liquor and store excess liquor to balance the flow. Typical equipment included are sand separator and in-line drainer, which remove sand, heavy impurities and shives and small chips from the liquor flow. Liquor surge tank balances the flow within chip tube. (Knowpulp, 2019)

4.2.4 **TurboFeed**

TurboFeed does not include low-pressure or high-pressure feeder, but apply chip metering screw, chip chute and chip pumps, typically three installed in series, to increase the chip and liquor mixture into sufficient pressure, without high-pressure feeder. These special type pumps are used to transfer mixture into the pre-hydrolysis, impregnation or digester. Larger quantity of liquor is used to provide sufficiently low consistency for pumping. Chute circulation is applied normally, but liquor is fed into the chip chute, instead of high-pressure feeder. (Knowpulp, 2019)

4.2.5 **Top circulation**

Top circulation means liquor circulation between top separator and high-pressure feeder or chip chute. High-pressure pumps increase the pressure of top circulation liquor before feeder to high-pressure feeder's pressure, from where it continues to top separator with chips and

liquor is extracted again in top separator to refeed into top circulation. Liquor-impregnated Chips continues to pre-hydrolysis, impregnation or cooking from top separator. Part of new white liquor is fed to top circulation to replace lost liquor. (Knowpulp, 2019)

4.3 Pre-hydrolysis kraft process

Based on the latest installations, Pre-hydrolysis Kraft (PHK) process has been more popular in new plants, especially in fast-growing China, where 78% of new installed capacity (new mills) is being based on PHK process. PHK in general is described as more of a capital project and more chemical consuming process, with more options for raw material and environmental compatibility. (Biermann, 2018) Quick progress is being done with development of hemicellulose and impurity extraction for PHK process, due to high growth rate in the popularity of the process meaning increasing market for process improvements as well. Other major development concept worth mentioning has been integrated bio refinery concept in which one mill would be potential producer for several outputs providing for demands of many industry sectors and end-customers.

On process level, PHK process combines both acidic pre-hydrolysis and alkaline kraft cooking. PHK process begins with pre-hydrolysis, which is essential to extract hemicelluloses from wood raw material. Most of the hemicelluloses that are extracted in the process are being removed in pre-hydrolysis stage. After pre-hydrolysis traditional kraft cooking with sulphate is performed, making it easier to integrate several outputs in comparison with acid sulphite (AS) process for modern biorefineries. One of the leading trends of dissolving production capacity increase is result of conversion of existing mills to dissolving pulp production. Change from traditional paper-grade pulp production is done with PHK process and adding extraction cycle (pre-hydrolysis) prior to cooking. Conversion can be purely from kraft to pre-hydrolysis kraft or option of swing line can be implemented, which makes it possible for mill to change between production of traditional paper-grade and dissolving grade pulps.

Reactivity of PHK pulp can be improved with cellulase treatment. (Miao et al., 2014) Displacement batch cooking technologies, as well as retrofitted pre-hydrolysis reactor

vessels have been the latest commercial applications bring additional value for producers of kraft pulp. (Biermann, 2018)

4.3.1 Pre-hydrolysis

Pre-hydrolysis takes place in separate pre-hydrolysis vessel (PHV) or within the top of the digester, depending on the mill and process layout. Hemicelluloses are extracted mainly on pre-hydrolysis phase and part of lignin is also separated. Pre-hydrolysis is essential part of PHK process, because together with sulphate (kraft) pulping, it removes most of the hemicelluloses without breaking long cellulose fibres, giving it high strength properties, and creating a uniform raw material for further processing. Optimizing pre-hydrolysis phase is economically viable to save bleaching or enzymatic chemicals in further process phases.

Extracting pure, solute hemicellulose sugars can also bring benefit to pulp mill in form of new side stream products. For example, extracting hemicelluloses converted to sugars, which can then be further refined into ethanol with fermentation. (Bajpai, 2012) The hemicelluloses and the potential end-products shall be discussed in later stages of the thesis. The outputs from the pre-hydrolysis phase are pre-hydrolysed wood chips that carry on to digester and pre-hydrolysis liquor (PHL) that contains hemicelluloses and other valuable extractives that can be further refined within mill site.

It is also possible to create a dissolving pulp fiberline without separate pre-hydrolysis vessel. While saving some process equipment and potentially maintenance costs initially, this however causes limitations of extraction possibilities and might cause issues in controlling pH and temperature of the process, which in turn can affect retention time and stability of pulp quality. All in all, not having a separate vessel for pre-hydrolysis can lower the sales profit in form of more poor pulp quality and increase chemical consumption due to additional cooking chemical usage. If pulp quality is insufficient after treatment of pulp in washing stages additional purifying stages can be needed. In separate pre-hydrolysis vessel, it is easier to extract hydrolysate and to decrease alkali charge going into digester, whereas in single-vessel system this controlling has to be made within the same vessel, and results in difficulties with control of H-factor over digester and also possible scaling within digester

and screens. (Vehmaa, 2019) H-factor is used to describe the delignification rate over cooking process, with variables being temperature and time.

Pre-hydrolysis process can use two main methods for hemicelluloses extraction, autohydrolysis or acid catalysed pre-hydrolysis. In autohydrolysis breaks part of wood's own hemicelluloses using acids naturally appearing on the wood, among other reactions. Autohydrolysis phase releases acetic acid bound on hemicelluloses, which lowers the pH to a range of 3-4. This is the primary driving reaction for hydrolysis and further breaking of hemicelluloses without weakening important structures of the pulp. (Bajpai, 2012) Depending of raw material, water-based inhibitor can be sufficient, or it can be boosted with small doses of chemicals. In increasing popularity, water-based autohydrolysis is used to lower the charge of alkaline in process. Development of pre-hydrolysis process is strongly favouring this trend when improvements are considered, and it will most likely be dominant technology in future fiberline installation and modifications over acid-based technology. PHL in water-based hydrolysis is also free of additional acids making the processing easier in case hemicelluloses are extracted for chemical production and recovery.

Using added acid for pre-hydrolysis increases chemical consumption of the mill and increases the chemical load of pulp production, increasing the importance of following the chemical circulation within the mill. Costs of pre-hydrolysis equipment can also be increased due to corrosive chemicals used in acid pre-hydrolysis. However, the acid catalysed pre-hydrolysis boosts the pre-hydrolysis process and lowers the treatment costs in other phases, such as bleaching and additional hemicelluloses extraction stages. At least sulphuric, phosphoric, and oxalic acids have been studied for the applicability for the pre-hydrolysis process. (Gütsch et al., 2012) Processing time can potentially be shorter than with autohydrolysis-based process due to stronger acid load giving flexibility for cooking process potentially eliminating bottleneck of early cooking stages.

Optimal pre-hydrolysis gives good basis for further kraft cooking. However, too extreme pre-hydrolysis with sub-optimal circumstances will have a negative effect to pulp quality by breaking cellulose structures wanted to maintain in end-product, potentially lowering reactivity or alpha cellulose content i.e. lowering the quality of wanted output. If instead of

regular hydraulic hydrolysis, steam pre-hydrolysis phase is applied, water extraction or acid hydrolysis has been applied, to reach desired pulping properties and conditions. In general, water pre-hydrolysis has been more efficient for hemicelluloses removal than steam pre-hydrolysis for both softwood and hardwood. (Bajpai, 2012)

4.3.2 Pre-hydrolysis methods in biomass and dissolving pulp production

Hydrothermal pre-treatment is used practice not only in pre-hydrolysis of dissolving pulp, but in bio refining in general. Typical pre-hydrolysis methods include steam explosion and hot water treatments. Steam explosion was the most used pre-treatment has been used in other biomass-based refining, and it uses medium to high pressure steam for relatively brief period. Steam penetrates the chips to result auto-hydrolysis reaction in wood chips just like hot water treatment, but after gassing the chips with steam, a rapid reduction of pressure is performed. Steam explosion is very low energy-consuming process, but it makes it more difficult to refine the hemicelluloses after the treatment due to lower disruption rate in structure of lignin-carbohydrate, which makes in incompatible with modern biorefinery concept. The steam explosion methods make it necessary to remove inhibitory compounds from woody biomass such as produced micro-organisms and enzymes, that would disturb further enzymatic treatment. (Saka, 2016) However, steam explosion has been used at least in studies to prepare for Organosolv cooking of eucalyptus, making it potential raw material and pre-treatment for Lyocell process. (Martino, 2017)

Hot water treatments include super- or subcritical water treatments and hot-compressed water treatment. Subcritical water means water below critical pressure or temperature. Hot water treatment makes it possible to extract different sugars, and maintains the condensed lignin structures well intact, therefore giving an option of selective pre-hydrolysis. Typically used flow-type supercritical water pre-treatment still makes it impossible to harvest part of sugars due to fragmentation of cellulose whereas subcritical water lowers the decrystallization rate of cellulose or lowering its reactive properties. Combination of both sub- and supercritical treatments make it possible to harvest carbohydrate products from hydrolysate with lower fragmentation rate. In hot-compressed water treatment severity levels of different stages can either depolymerize cellulose (unwanted reaction in dissolving pulp

production) on higher temperatures and increase the carbohydrate extraction on lower. (Saka, 2016) Pre-hydrolysis used in dissolving pulp production typically uses lower temperatures and longer reaction time to limit the structural changes in cellulose portion.

4.3.3 Kraft cooking process

Leaving from pre-hydrolysis, the pH value of pulp is between 3-4. In kraft cooking phase, extraction of lignin is the primary target. Lignin solutes to cooking liquor rich in caustic soda hydroxide and sodium sulphite, called white liquor. Cooking temperature and pressure are typically between 140-170 °C and pressure under 10 bar. Both existing and new continuous (CC) and batch cooking (BC) lines can be applied to produce dissolving pulp. Traditional CC process can be converted into pre-hydrolysis kraft process by adding pre-treatment vessel into feeding prior to digester. In continuous cooking pre-treatment of chips is done with retrofitted separate pre-hydrolysis vessel (PHV). In batch cooking integrated pre-hydrolysis is used. Practically any of the continuous digester cooking models can be used to produce dissolving pulp. After kraft cooking, multi-phase bleaching is applied to achieve the required brightness and purity according to market and specified buyer standards. (Chen et al., 2016) Pulp is pushed from digester to blow tank after cooking is done.

4.3.4 Bleaching

Bleaching is the stage where final brightness and purity for pulp is reached, after bleaching pulp is dried for transportation to end-users. Especially in dissolving pulp production, sufficient purity directly affects the yield and chemical consumption in production. When talking about bleaching, two major categories are often separated, elemental chlorine free bleaching (ECF) and total chlorine free bleaching (TCF). Several stage bleaching is normally applied, and there are many commercial methods to do it, however it is always a combination of reaction vessels and washing equipment, where pulp is washed (and water is removed), preparing the pulp for next bleaching stage.

The layout of bleaching and number of stages always depends of the required purity for end-product, as well as raw material, dry matter content and most importantly quality of cooked wood chips (pulp) after digester. For hardwood material, the number of bleaching equipment

or chemicals can be lower than for softwood due to better bleachability. One stage always consists of chemical reactor and washing equipment. Reactor is used to mix the pulp and bleaching chemical, and washing equipment can be either diffuser, filter, drum washer or press type, and the main function is to remove impurities from mass with the help of chemicals and/or wash the pulp with water. Some water is also removed during the bleaching no matter which technologies is used, so dry matter content is higher at the end of bleaching. Modern mills typically run higher dry matter content than older mills on bleaching and even in brown stock washing, which might limit the use of certain bleaching technologies or make them more inefficient.

EFC bleaching stages can include one or several oxygen delignification (O₂), peroxide (P), ozone (Z), chlorine dioxide (D) or reinforced alkaline extraction (EOP) phases. TCF or oxygen chemical bleaching does not apply chlorine dioxide phases, so usually pressurized peroxide (PO) is used as final bleaching stage. Peracetic acid (Paa) and activated acidic peroxide (mP) stages are also applicable in TFC bleaching in earlier brightness stages. (KnowPulp, 2020)

As discussed above, required brightness depends on end-use, being highest on viscose, lyocell and acetate raw material. Residual lignin affects not only for brightness, but also for processability. Processability of dissolving pulp quickly lowers if residual lignin content is left above 0.17%. (Sixta, 2006)

4.4 Pulp purity prior and after the kraft-cooking process

Lignin is generally not an issue after kraft cooking process as alkaline cooking conditions extract lignin from wood effectively. Improvement of pulp quality around pre-hydrolysis kraft cooking process is focused on further extraction of hemicelluloses and improving the structure of cellulose itself. The processes applied to reach dissolving quality pulp are

- Treatment with chemicals
 - IONCELL or other ionic liquid extraction
 - Hot or cold caustic extraction

- Organosolv extraction
- Treatment with enzymes
 - Xylan or mannan extraction with xylanase and mannanase
 - Laccase treatment phase
- Combination of enzymatic and caustic extraction
- Mechanical refining
- Microwave (Biermann, 2017)

Post-treatment of dissolving pulp is done to ensure the high purity of pulp. Post-treatment can also replace the pre-hydrolysis completely to give sufficient level purity, however the insufficient pre-treatment lowers the overall effectiveness of cooking. Impurities, such as left-over hemicelluloses (especially xylans and mannans) in dissolving pulp can cause several issues in later refining stages, such as weakening of strength properties of product, and other critical properties like reactivity or cause false viscosity and filterability. (Sixta, 2006)

Several studies have led to conclusion that insufficient purity during refining, cooking and pre-hydrolysis stages of dissolving pulp lead to issues, namely excessive consumption of chemicals, issues with plugging of nozzles during rayon production, discoloration of end-product and generally lower the yield. These can all be reduced or eliminated with proper pulp treatment methods. (Chen et al., 2016)

There are methods of extracting hemicelluloses prior and post cooking. In comparison to PHK cooking, acid sulphite cooking performs both lignin and hemicelluloses removal in same stage, but in pre-hydrolysis kraft cooking hemicelluloses are left in pre-hydrolysis kraft pulp. This is also one the reason extraction technologies are being developed. Technologies that can be implemented after cooking for hemicelluloses removal from liquor are cold caustic extraction (CCE), hot caustic extraction (HCE), acid extraction, enzymatic treatment

(to remove specific hemicellulose components), mechanical processing and other methods, such as using metal complexes in extraction.

4.5 Chemical treatment

4.5.1 IONCELL process

IONCELL process can be applied to pulps regardless of raw material or process, but it offers primarily an option for selective hemicelluloses removal. In current market, it has two main applications. Traditional paper-grade pulp has high hemicelluloses content, but lignin is removed quite efficiently with kraft cooking, although with high loss. IONCELL process can give mill an option to convert the production directly with support of kraft cooking equipment from paper-grade pulp to standard quality viscose-grade pulp production. (Sixta, 2013) This also makes it possible to produce both qualities within the same mill and possible fight against fluctuating prices of paper-grade pulp in the long run. Other option is to go even further with refining of pulp, adding phases, like enzymatic and acid treatment to produce higher-purity pulps, to produce even higher refined products such as acetate-grade pulp, exemplary flow chart can be seen in Figure 3, where different purification processes with varying process phases. This has been studied by Roselli et al. in 2014.

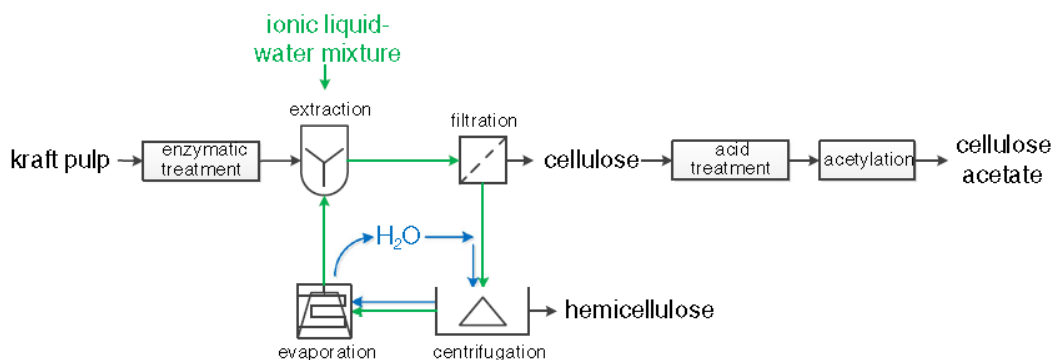


Figure 3. Flowchart of IONCELL process (Roselli, 2014)

IONCELL process involves mixing the bleached kraft pulp mass in an ionic liquid solvent system and press filter (with metal fleece of tiny pore diameter) is used to separate

(undissolved) solids from (solved) liquid. Mass consisting of solids is washed and dried, giving output of pure fibre-rich cellulose. Solvent is dissolved hemicelluloses, which is precipitated with addition of water. Used solvent in commercial application is recycled to fractionation process, which reduces chemical consumption over the process. (Kumar, 2017) Several ionic liquids have been tested and used, as they are commercially available solvents.

4.5.2 Cold and hot caustic extraction

Cold caustic process uses alkali concentrations of typically 8-10 % and temperatures of 20-40 °C to extract selected hemicelluloses, especially it has been applied to xylan removal for hardwood paper pulps in direct conversion from paper-grade to viscose. In general, it can be said that higher the temperature of CCE, the higher the extraction rate of hemicelluloses, but high temperatures also affect the degree of polymerization in lowering manner, which is not favourable for dissolving pulp. CCE cannot, however, be used to extract glucomannans in sufficient manner. Therefore, additional hemicellulose extraction phases should be used in combination, such as peeling. CCE is better suited for Acid-sulphite process due to this highly selective in terms of xylan removal. (Bierman, 2018)

Hot caustic extraction has NaOH loads of only 0.4-1.5% and has elevated temperature in the range of 95-135 °C. Similar swelling as in CCE does not happen due to low alkali load, which leads to lower hemicelluloses extraction rate, and lower yield. (Biermann, 2018) Another option for effective hemicellulose removal would be acid treated pulp followed by hot caustic extraction with higher NaOH load. A-HCE treated pulp has higher reactivity, but lower degree of polymerization due to the acid treatment. This combined A-HCE -method has been studied by Arnoul-Jarrialt et al. in 2015. A-HCE method is suitable for PHK process, due to high extraction of alkaline-resistant hemicelluloses. (Biermann, 2018)

4.5.3 Enzymatic treatments

Typically, in PHK process, hemicelluloses are removed during pre-hydrolysis phase, but selected carbohydrates cannot be easily extracted, as they are not easily accessible or form complexes, that are not split by pre-hydrolysis liquor. Selective enzymatic post-treatment to remove hemicelluloses has also been studied, showing that effective enzymatic treatment

would be to combine mannanase and xylanase to remove hemicellulose efficiently. (Gübitz et al., 1999) These hemicellulose enzymes are applied usually only in bleaching stages.

Another enzymatic treatment that has been found beneficial to remove lignin in pulp prior to bleaching is laccase treatment. Cellulase treatment has been noted to boost reactivity by increasing porosity of fibres, making it optimal for PHK process. (Biermann, 2018) In combination with violuric acid (VA) and pressurised peroxide (PO) bleaching stages, it was noted to aid in reducing chemical consumption without degrading cellulose or weakening the properties of dissolving pulp, making it potential sequence in combination with other bleaching stages in production of commercial dissolving pulp. (Quintana et al., 2014)

4.5.4 Cellulose-based nano composites

Micro fibrillated cellulose (MFC), that is used for example in thermoplastic polymer and composite processing and fortifying these materials, can be produced by using shearing force and mild enzyme-boosted hydrolysis. In MFC production weaker parts of natural cellulose fibres removed by using mechanical shearing and mild enzyme-based hydrolysis, removing weaker, non-crystalline parts, leaving crystal aggregates intact. Other method is to leave out the traditional hydrolysis step and using mechanical shearing forces and mild enzyme-boosted hydrolysis. (Eichhorn, 2010)

MFC contains nanofibril aggregates, and cellulose nanocrystals (CNC) are individual nano whiskers of these nanofibril aggregates when it has been fully processed. Several technologies have been implemented for CNC production. Most common is acid hydrolysis to cellulose nano whiskers to break form original aggregates. High yield but long process time has been achieved with enzyme-based hydrolysis combined with ultrasonication. Water hydrolysis and mechanical processing has also been reviewed for CNC production. (Thompson, 2019) Main resource for fibrillated cellulose, independent of production method, is cotton because high intensity of purification will evidently lead to lower yield and weaker material properties that is the key factor for its end uses. (Eichhorn, 2010) Higher uniformity, or length of crystals can be achieved with cotton-based CNC as well.

4.6 Mechanical treatment

Mechanical methods to affect structure of cellulose include refining, milling, and shredding. They are most useful in processes where penetration of chemicals and low reactivity (due to low porosity) of cellulose can be an issue, namely PHK process. (Biermann, 2018) Several studies have been performed of combination of mechanical and chemical treatments, especially in PHK pulping, included lowering alkali concentration with mechanical refining and cold caustic extraction. (Li et al., 2015) As discussed above, mechanical treatment has also been applied for production of cellulose nano crystals.

4.7 Qualification and properties of dissolving pulp

Dissolving pulp quality is measured in following parameters; reactivity, alpha-cellulose content, alkali solubility, degree of polymerization (DP) and molecular weight distribution (MWD). There are different methods to achieve required or target purity, including selection of wood species and usage of different production processes, (Chen et al., 2016) as well as adding pre-treatment phases prior to cooking and extraction phases after cooking.

Properties of dissolving pulp have been given a lot of attention in last years, because the quality of pulp directly affects costs and environmental impact of refining the end-product and insufficient parameters can even limit the applications where pulp can be used. Especially reactivity has gained a lot of study, because pre-hydrolysis kraft (discussed in chapter 4.2) pulp being the 'softer' method to cook dissolving pulp can have issues with lower reactivity compared to acid sulphite pulp (chapter 4.3). This is because PHK process cannot affect molecular weight i.e. it is not able to cleave through the cell wall, and boost reactivity as well as AS process can. It has also been studied that reactivity of hardwood is lower in comparison with softwood pulp even within the same process. (Duan, 2015) Further reasons behind difference is discussed when these cooking methods are introduced. As discussed in IONCELL chapter above, cellulose output directly from kraft pulp process is insufficient and has high degree of impurities namely hemicelluloses, that can require special extraction phases.

4.7.1 Characterization

The lowest quality of dissolving pulp is used for textile industry, regenerated fibres and films. Higher purity specialized pulp producers have optimized their process to produce higher purity pulp for more specialized end-uses. These include esters, ethers, micro- and nanocellulose and others. As discussed in early chapters, it is not economically viable or wise to refine the purity of pulp higher than necessary as this will increase costs and energy consumption per ton of pulp. Therefore, there are some measurements that normally define the required quality of pulps.

Parameters used to classify dissolving pulp quality are essentially related to processability of pulps after bleaching. The most common unit is pulps intrinsic viscosity, according to SCAN-CM 15:99, and Kappa number, according to SCAN-C 1:100. Other important qualities are alkali resistance R10 and R18, giving the value of how much of the dissolving pulp is insoluble in 10% NaOH or 18 % NaOH solutions. This gives an idea of the purity of the pulp is because only hemicelluloses and lignin is dissolved, and pure cellulose is maintained relatively well intact.

Other important parameters can be described as more end-use specific. Degree of polymerization DP describes the content of short fibres within pulp, describing its initial strength characteristics. Typical unit used is DP <100, that gives value of how large portion of fibre in pulp is below the molecular weight compared to anhydroglucose unit. Larger content of short fibres means weaker strength characteristics in refining. Unwanted organic contents can also be sorted by each subcategory, as leftover hemicelluloses, acetone extracts or lignin. The parameters are further described and discussed in Christoffersson's dissertation from 2004. (Christoffersson, 2004) Brightness of the pulp is the final parameter after last bleaching stage, and it can be measured in ISO %-scale. Bleaching sequences had drastic effect on viscosity, especially on PHK pulp lowering it quite much but not as much on AS pulps because the initial viscosity is typically lower on AS pulps than on PHK. (Sixta, 2018)

4.8 Acid sulphite process

In AS process, the extraction of hemicelluloses is done in the same phase with lignin removal. Chemicals used in pulping process consists mainly of solutions of sulfur dioxide and hydrosulfites. In the process, acid is responsible for removing or breaking the hemicelluloses present in pulp and sulphite compounds breaks through lignin.

AS process increases reactivity of dissolving pulp by effectively breaking through the primary wall and creating optimal conditions for penetration of bleaching and possible treatment chemicals. However, molecular weight distribution is higher due to this destructive nature of AS cooking, which limits the end-uses where uniform structure is needed. Longer molecular chains can also break down, lowering the weight distribution in comparison to softer PHK process. (Bajpai, 2012)

In acid sulphite process, the acid works as hemicellulose-removing agent, whereas in sulphate process, an additional pre-hydrolysis phase is needed to remove hemicelluloses from cooking flow. Even when using these additional steps or sulphite cooking, small amounts of hemicelluloses, especially parts of xylan are left to pulp, later possible causing issues in production of rayon or other quality issues for products. (Bajpai, 2012) Effective methods to extract xylan have been introduced in previous chemical treatment chapter, especially cold caustic extraction can be used to extract xylan without lowering degree of polymerization. Implementation level of CCE is higher in AS process, where as in PHK more selective technologies are being used.

Similar issues are caused by impurity in both PHK and AS cooking. Such issues can be filterability of viscose, xanthation of fibres in later process steps or even weakening the strength of final products in viscose production. For complete removal of xylan, enzyme treatment has been applied to remove xylns from pulp without affecting cellulose fibres. Since kraft pulping is more common process for dissolving pulp production, studies related to sulphite process enzymes have been very limited. (Bajpai, 2012)

Three main flows can be noted from AS process, cellulose pulp, monomeric sugars and lignosulphate. In AS pulping the quantities are usually large in each of three categories,

making it profitable to produce several different value-added products to increase profitability. (Sixta, 2013)

4.8.1 Xylanase use for hemicelluloses extraction

As the issue of poor reactivity of xylan has existed for prolonged time in the AS pulping process causing issues, xylanase usage (enzyme to break leftover xylan in pulp into xylone) has been applied into kraft pulping. First industrial tests have been performed in mid-1980's. As reference point, in 1994 around 8 % of Canadian bleaching mills used enzymes to enhance the pulp purity. (Christov, 1999) Ideal enzyme for xylan removal should not influence other components of pulp mass or affect the molecular weight of pulp. (Bajpai, 2012) Christov has also studied use of strains of white-rot fungi (xylanase) in both unbleached and bleached dissolving AS pulp production as both pre-treatment method and additional (bio)bleaching chemical in 1999.

It was noted that use of Xylanase from nature to pre-treat AS pulping raw material or additional xylanase into bleaching stages improved yield, lowered chlorine consumption and improved brightness of pulp. Both of these factors improve the economic and environmental aspect of produced dissolving pulp. Namely potential improvement with use of xylanase could be lowered oxygen demand for effluent treatment, lower chemical consumption, improved yield and pulp quality and marketing advantage for bio-pulped or bio-bleached pulp. Issues with xylanase use are related to corrosion of equipment and issues with controlling the bleach plant. Development has been made for pH and temperature balances and improving competitiveness of xylanase prices versus other enzymes used in pulping and bleaching. (Christov, 1999)

For pre-treatment (in bio sulphite pulping), wood chips were pre-treated for one week with several strains of white-rot fungi, as different tests samples. Most notable impact was noted with *Ceriporiopsis subvermispora* SS-3, which lowered kappa and improved brightness without notable lowering yield of unbleached pulp. During the bleached pulp testing the correlation between unbleached and bleached pulp was dismissed as the yield in comparison to control was increased. (Christov, 1999) Therefore, it might be suggested to use fungi-based enzyme for bleached pulp production, rather than unbleached pulp.

In comparison to reference sample, one-stage peroxide bleachability was improved for (lower) Kappa and higher brightness achieved for all tested enzymes. In multi-stage bleaching it was noted that bio bleaching positive effects gets declined with several bleaching stages. The load on active chlorine stages could be reduced by 33% and 50%, in D₁ and D₂ stages respectively, when using multi-stage bleaching with peroxide and oxygen extraction stages, which notably lowers the impact on chemical consumption and environmental aspect. (Christov, 1999)

4.8.2 SEW process

Another option to fractionate hemicelluloses from cellulosic raw material is SO₂-Ethanol-Water process, SEW in short. It could offer new side stream products for integrated biorefineries because hemicelluloses (hydrocarbons) are not destroyed during extraction process, which means they can be extracted as side products. The recovery rate is higher than currently dominating production methods, PHK and AS processes. (Iakolev et al., 2014) Currently, in traditional PHK steam pre-hydrolysis, hemicelluloses that as extracted are only neutralized and burned with lignin, which doesn't offer added value to mill other than being combustible fuel to reduce external heat demand. Hemicelluloses heating value is also much lower than lignin, and therefore alternative combustible materials would be preferred over potentially valuable renewable polymers. (Sim et al., 2012)

When comparing the SEW produced pulp bleachability wise to AS pulp, initial indication suggests it to be close to AS pulp properties, except for OXE (oxidizing equivalent) which seemed much higher than in compared AS pulp. (Iakolev, 2014) OXE describes the amount of bleaching chemical consumption required to reach desired purity, being higher on oxygen-based chemicals and lower on acid or chlorine-based chemicals. (Sixta, 2006) Actual viscose production from SEW pulp has not been piloted, but laboratory tests suggest it to be reactive. Properties after bleaching were found to be close, but during pre-bleaching notably high kappa number was found on SEW pulp, which has probably resulted in higher requirement of OXE, because in cooking optimal kappa number to reach minimized bleaching and oxygen delignification plant load would be much lower than achieved in laboratory tests. (Iakolev, 2014)

4.9 Comparison of Pre-Hydrolysis and Acid Sulphite processes

It can be described that dissolving pulp from PHK process has lower reactivity in comparison to dissolving pulp from AS process, but PHK has more uniform molecular weight distribution. This makes PHK process a desirable choice for end-uses when uniformity is highly valued. PHK process has also been noted to be better at removing extractives, due to the separate alkaline cooking stage. (Chen et al., 2016) Reason for lower reactivity in PHK process is the fact that unlike in AS process, own acidic compounds within the wood is used to cleave the hemicelluloses. Constant quality and extraction potential makes PHK preferred technology for integrated biorefinery. For both processes possibility to extract value-added chemicals has been developed lately. Value-added chemicals here means separation of hemicelluloses, sugars and other chemicals that can be sold or used in the processes other than combustion. Higher alpha cellulose content is typically achieved with PHK process, however PHK pulp also contains little more hemicellulose than AS pulps.

In energy and environment sense, PHK has very good points over AS process. Long cooking time and consumption of cooking chemicals in AS cooking increases energy and operation costs. In AS process, additional acid compounds are brought to cooking outside of process, and reactivity is higher than in PHK. However, auto-hydrolysis process in PHK environment can be more easily controlled and most of the lignin is extracted on later stage in alkaline cooking. Acidic compounds formed from woods own compounds does not break the primary wall of cellulose, and in PHK process primary wall is only partially destroyed. In AS, more of celluloses primary wall is destroyed due to stronger cooking process. In more precise description, it has been quoted as “intensive cleaving” for AS process and “stepwise peeling” in PHK process by Duan in 2015. AS process therefore provides higher viscosity, more accessible raw material and during xanthation AS pulp reacts better, but variation within raw material can cause issues with machines. (Duan, 2015)

4.10 Cotton linters in dissolving pulp production

Cotton linters are the raw material of highest degree of pure dissolving pulps, generally meaning over 99 % of alpha cellulose content. Raw material for the production is separated

cotton linters during production of cotton seed oil. As the raw material cotton linters has the highest natural alpha cellulose content out of three main branches of dissolving cellulose fibre production, it is the primary material for high-purity applications. Production of cotton linters begins with delimiting of cotton seeds, and proper fibres with optimal length are treated with combination of chemical and mechanical steps to remove unwanted parts and increased the purity and brightness of pulp. (Sixta, 2016) Process steps are fewer and less aggressive on raw material due to the natural high content when comparing to wood-based raw material. This means the yield per ton of raw material is fairly high. Due to demand in high-end cellulose use means higher raw material price, even when being side product of cotton seed oil production.

As discussed, the part of all dissolving cotton linter pulp is around 10 % of all dissolving pulp, so some mills are producing cotton linter-based pulps around the world. When targeting the alpha cellulose content of over 99 %, cotton linters are currently the most economic choice with much fewer refining process stages than in comparison with wood-based dissolving cellulose. However, advances in processing wood-based dissolving pulp is bringing the costs closer to cotton linter, but selectivity of wood-based process must be enhanced further to reach economic state of high-alpha being as profitable as cotton linters.

4.11 Selection of process and limitations

Selection of process depends on several factors, such as available raw material and its limitations to cooking process, required end-product quality and attributes. Limitations can also be set by further extraction phases, which can affect the yield if too strong bleaching or hemicelluloses extraction is used. Insufficient hemicelluloses and/or lignin extraction can cause issues in xanthation or in further refining. It is also noteworthy that insufficient cooking and pre-hydrolysis will result in increase of consumption of energy or chemical usage for bleaching and purifying process.

For PHK process, high non-cellulosic compound is not recommended, however they can be used. This is because cellulosic extractives (side products) are extracted from pre-extraction liquor and high non-cellulosic means lower content of these extractives in PHL and this will

increase the cost-per-unit. Bottlenecks are typical on PHK mills, and low-cellulosic content directly means lower capacity for the mill. There are also other more suitable low-cellulosic cooking methods, that do not convert very well into dissolving pulp production, such as organosolv process. All in all, it would be recommended that with current technologies high non-cellulosic raw materials would not be used for dissolving pulp production.

Acid sulphite process has some limitation of wood raw material due to certain compounds reacting with lignin. These include raw material with certain phenolics (pinosylvin, taxifolin, flavanons) and extractives (tannins), that can cause issues in AS process. These extractives tend to react with lignin in the wood and form cross-links that cause severe issues in the further process. (Sixta, 2018)

4.12 Cooking layout

Cooking layout for dissolving pulp cooking can be either build on existing kraft pulp fiberline or designed based on planned dissolving pulp production. It is typical that existing equipment is left on site so that mill can produce both dissolving pulp and paper-grade pulp. This sort of arrangement is called swing line. One of the most typical layouts for swing line is to use single-vessel cooking with digester only for paper-grade pulp production and include the use of pre-hydrolysis vessel when dissolving pulp is produced. Swing line increases the potential customer base and provides economic stability in case variation between dissolving pulp and kraft pulp occurs.

It is always preferred to have some level of impregnation for chip before introducing the chip to cooking liquor. There are some ways to achieve this, older mills having pre-steaming screws, implementing steaming into chip bin before chip pumps or feeders and impregnating chips in digester top. There are some of studies that impregnation is one of the key factors of successful cooking and reduction of reject after digester and a key factor when aiming for low kappa pulp in paper- or board-based mills. (Malkov et al., 2001 & Ningpan et al., 2016)

4.12.1 **Visbatch cooking**

For batch mills, Visbatch cooking method is relatively close to traditional displacement cooking, with medium pressure steam prehydrolysis integrated in the same vessel. Sequence continues with black and white liquor neutralizing of chips and hot displacement is performed as in typical displacement batch cooking. After heating and cooking sequences cold displacement takes place, where washing filtrate is pushed into the digester, and cooking (black) liquor is pushed into warm and hot black liquor tank for continued displacement. Pulp is discharged from digester to blow tank and new chip filling takes place. White liquor is heated with spent liquor from previous cooking, reducing the steam/energy consumption within mill. Fairly good results have been achieved, with energy saving and chemical recovery, with R18 values around 94 %, being around 96 % for typical continuous digester process. (Wooding, 2001)

4.13 **Conversion of paper grade pulp to dissolving pulp**

Recent trends on pulp mills across the world has been increasing mill sizes with scaling the sizes of the equipment up and producing continuously larger quantities of pulp within one mill. Such line extensions have also been seen within existing mills, with drive to remove bottlenecks and optimizing process with as little investments as possible. Current situation where the global pulp making capacity has increased and demand for paper-grade pulp has been reduced, except for board production, combined with tightening competition of paper-grade pulp market has driven the price per pulp ton to drop drastically within the last year. From level of early 2019, prices of around 1200 dollars per ton of soft wood pulp, the decrease has been drastic, with early 2020 prices being around 800 dollars per ton. (Vision hunters, 2020)

Conversion is not a simple task, as it effects mass and energy balances of the mill. In general, dissolving pulp production has higher costs per unit of pulp, in form of wood and chemical consumption, and output received in lower than traditional kraft mill due to higher refining level. In general, average kraft pulp mill yield is over 43 % whereas average dissolving kraft pulp mill yield is only around 33 %. This means lower production per ton of wood is achieved for dissolving pulp than with paper grade pulp, making the support functions as

such wood handling or recovery boiler potentially critical or possible bottleneck for conversion. The amount of side stream products extracted can also be one of defining factors when considering the economic and technical solutions of modern swing line able to produce both dissolving and paper grade pulp. Some studies have been done about the bottlenecking, and it would seem the digester is often limiting the capacity. (Lundberg, 2014) Naturally, this would have to be studied case-by-case, but it could be something to investigate early on in possible conversion studies.

Other issues with conversion can arise from higher requirement of brightness for dissolving pulp, increasing chemical consumption and requiring potential improvements for bleaching line. (Biermann, 2018) Bleaching plant is also one of the typical bottlenecks and quality of bleaching also has high impact on product price and strength. Consumption of steam also increases with conversion to dissolving pulp production. This can result in bottlenecking of energy production as often mills are functioning on the optimized capacity of recovery boiler or lime kiln. This can result in demand of upgrade for boilers or other modifications of energy production and/or chemical recovery within mill, which means careful studies should be implemented before executing a conversion. Parts of increased steam production can be covered with extracted cooking liquor or extracted hemicelluloses with high energy output, that are not extracted in traditional paper-grade production, but this should also be compared to the potential sales price of side stream products rather than direct combustion of the potentially valuable raw material. Due to these extensive and potentially expensive expansion requirements, many studies have been performed to create more inexpensive process without requirement of rebuilding large areas on site but to rather chemically purify or refine the pulp. (Biermann, 2018)

4.13.1 Issue of bottlenecks

Due to the extraction of hemicelluloses in early phases of chip cooking, mass and energy balances within mill site change in comparison to traditional kraft cooking. Yield of dissolving pulp per tonne of chip is naturally lower than for paper grade pulp due to higher purity requirement with same raw material, so potential upgrade or improvement projects to counter the bottle necks within mill would be typically removed to maximize profitability of

the mill. On mill level this issue with lower output with same amount of raw material leaves two options, a) to inspect the capacity of each area of the mill considering potential new mass balances and upgrade the insufficient areas to upgrade their production or b) run the mill on bottlenecked mill, producing dissolving-grade pulp on lower (or maximum) output. Depending on the primary production, mill strategy and intentions, both of given options can be valid decisions.

Higher raw material requirement per product also means larger side streams on mill which can in turn mean vast upgrade requirements depending of capacity of each critical parts of the mill. Side streams can be combusted and used for energy production, or alternative option is extracting side products from pre-hydrolysis liquor for added value per raw material. (Lundberg, 2014)

4.13.2 Extraction of side products and Pre-hydrolysis liquor

The potential of dissolving pulp mill, currently regardless if main process is AS process or PHK process, conversion into biorefinery with high efficiency and added value for mill with extraction products can provide added value. It is also a known issue that pre-hydrolysis liquor has high oxygen demand, so disposal by natural means would have high impact. Combustion would be option, but due to low consistency it is not very economic. (Silva, 2018) The concept of biorefinery within mill site has gained a lot of attention and studies lately and in any conditions refining value-added chemicals is more economic than combustion. Instead of boosting capacity and increasing capacity of mill, already in mill design phase it can be very economical to consider what extracts it would be extracted from PHL to evaluate total value of production chain.

One way to measure the added value is to compare the sales profit versus handling costs and potential value when existing end-use is applied. For example, on regular kraft pulp mill lignin can be either combusted or sold. Extraction of lignin is possible with added process equipment, so only potential issue is lower heating value and mass going into recovery boiler. In PHK process, some studies have been made about extracting lignin from pre-hydrolysate with laccase treatment. (Mazar, 2018) If no additional cost or issues arises from extraction to combustion, the return of investment time can be estimated to be sales profit

versus investment on extraction plant. Naturally, it should also be noted that PHL can be mixed with black liquor from digester to increase output to black liquor recovery circulation, which is currently dominating trend. This can result bottlenecking in chemical recovery. (Silva, 2018)

Hemicelluloses harvested from pre-hydrolysate in PHK contain different hydrocarbons of varying amounts depending of the raw material resource and intensity of pre-hydrolysis. In figure 4 are some of the most potential options for mills to consider bio refinery-wise.

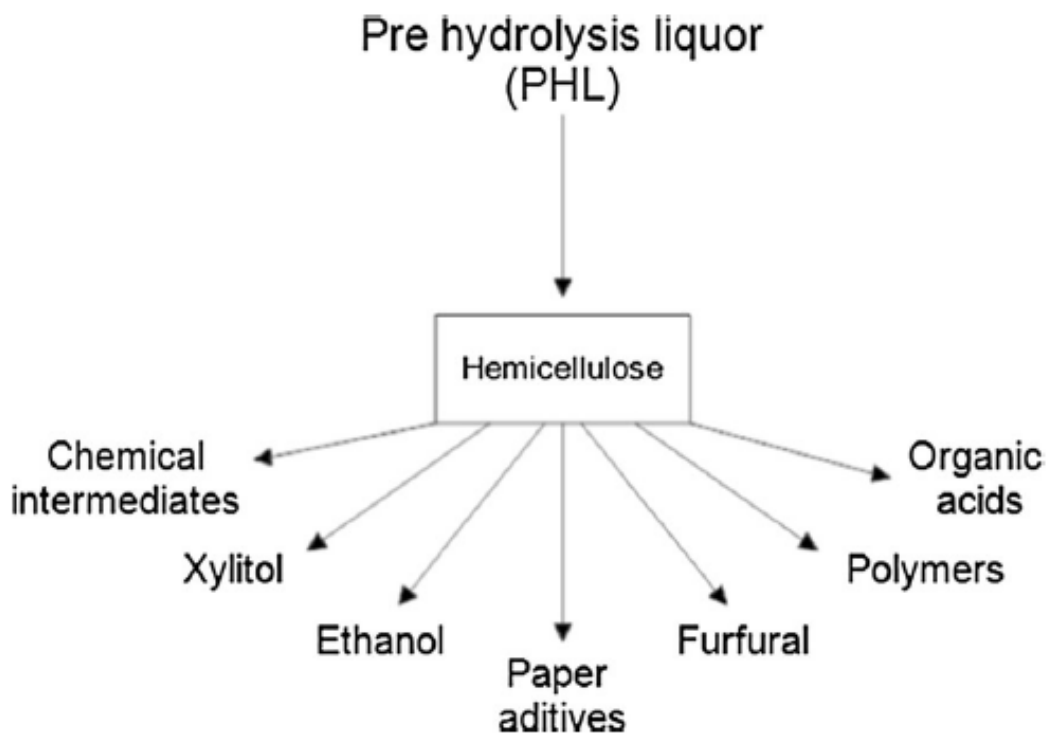


Figure 4. Potential conversion options for PHL hemicellulose value-added products. (Kumar, 2017)

Potential value-added in pre-hydrolysate include hemicelluloses, hexoses, and lignin. Recovery of lignin or refining of furfurals, ethanol, or xylitol can provide stability and improve the profitability of mill in general. Lignin has also been used as inhibitor during fermentative conversation of these other sugars, instead of extracting it as additional product. That means mill can benefit of it internally and there is no need to find external company to

supply the lignin. (Mazar, 2018) As long as lignin extraction has high quality, it can also be used in lime kiln to replace fossil fuels.

Typical options to separate these from pre-hydrolysate is use of flocculation agent and filtering it or acidifying the pre-hydrolysate and centrifuging it. Flocculating of pre-hydrolysate increases the molecular mass of very low molecular weight of untreated lignin in pre-hydrolysate. Mazar et al. (2018) has also studied lignin extraction with membrane filters in 2018, reaching high rate for both sugars and hemicelluloses retention with 1 kDa membrane.

It is possible to produce xylitol from pre-hydrolysis liquor with purification from xylose, and by hydrogenating with catalyst at increased temperatures of 80-140 °C and pressure of 50 bars. Increasing interest is gained by microbial fermentation, which gives same end-product with xylose reductase, which naturally produced enzyme. Ethanol is produced in large scale on several commercial applications. It also happens that many of the natural micro-organism cannot ferment sugars in PHL to ethanol or the rate of fermentation is too low to be commercially viable. Several other compounds present on PHL, such as lignin in high quantities and acetic acid, without pre-treatment might also inhibit fermentation process. It can also be difficult to extract the for-mentioned compounds efficiently from PHL, although they also have some end uses in chemical industry. It might be useful to detoxification or adapt microbes to improve opportunities for fermentation of PHL compounds. (Mazar, 2018)

Furfurals are present on PHL and can be extracted from acid hydrolysis and dehydration of monosugars. It has a variety of uses, from feedstock for production of resins to using as an intermediate in several sorts of synthesis of chemicals of different fields. Extraction of furfural with membranes and activated carbon has been studied, although it is currently harvested with the mentioned acid catalyst batch treatment. (Mazar, 2018)

4.14 Future of dissolving pulp and aspects

Dissolving pulp production has high potential in the future due to integrability to existing mills and possibility to extract side products from cooking liquor, making pulp mills become

more of a bio-refineries with several output to markets, potentially providing local resources to market for local mills to use, instead of providing them from thousands of kilometres away. It is also one of the key factors when moving from strongly fossil- and cotton-based textile industry to renewable sources as we know today. Even within dissolving pulp industry a variety of production methods are still used. It can be said that regular dissolving pulp production process has somewhat similar environmental and social effect as paper-grade pulp production, when leaving the xanthation part out.

One of the key issues of dissolving pulp is also strongly related to the environment. Most common xanthation processes (treatment after production of pulp) are toxic to humans and environment, as it uses CS₂ chemical in dissolving agent for pulp. Therefore, the production of viscose with these processes are banned in many countries around world. Commercial applications need around 32-34 % of CS₂ per weight-% to pulp weight-% for the process to be sufficient. (Gondhalekar,2019) Therefore, it is fair to say that process at current state is very poorly optimized and is causing excessive chemical consumption and unnecessary danger on viscose production mills. As CS₂ is very toxic to humans and environment, alternative process for xanthation should be searched or at very least, process should be studied, and process optimized to minimize the chemical used. Alternatives do exist but they are not in high-grade commercial use, such as Ioncell described in chapter 4.4.1 and Lyocell process, that uses amine oxide solvent.

This means, that many countries with high legal restrictions of xanthation and strong environmental policies can produce dissolving pulp from wood, when only a handful of countries have high potential in refining the pulp into viscose or products alike. Although production rates and consumption rates are soaring, this might make the production of dissolving pulp as we know today a political game, if methods of pulp refining are not developed to be available for countries with strong restrictions, meaning not developed to provide safe and environmentally safer pulp. At least the competitiveness of pulp will most likely suffer if new processes are developed and they are more expensive than currently dominating ones. Companies able to produce and sell equipment should have a leading role in moving from unstable and dangerous processes into safer and potentially more effective procedures in refining of dissolving pulp.

It is quite safe to say that with current trend, dissolving pulp production will increase to grow in popularity in the upcoming years and continue steady production increase on annual basis. Major dissolving pulp mill projects are ongoing globally and existing mills struggling with demand of paper-grade will see option of conversion as desirable option. On the other hand, demand for dissolving pulp has not yet seen notable decrease even with increasing production volumes all over the world thanks to swing line mills and continues global increase in demand for textiles. As the recovery demands for textiles and more and more mills turn from paper to textile raw material producers, this might influence demand in the future.

4.15 Nanocomposites for several fields

Nanocomposites of cellulose fibres and their production have been under intensive study in recent year. Their several beneficial characteristics over traditional alternatives justify the growing interest on several commercial applications. They are of renewable raw material, they are biodegradable, and biocompatible, non-toxic and provide greater material strengths, to name a few. For these and other reasons, their manufacturing consumes lower energy per weight unit and help reduce carbon emissions and due to lower abrasion lower the equipment maintenance requirements. (Kumar, 2017)

Several uses include paper industry, construction and building materials and food packaging, as well as biomedicine and cosmetic industry uses. In food industry, polymers have been used in coating of packaging applications in increasing volumes and with nanocomposites it is possible to reduce materials consumption by improving the structure and properties. Biopolymers (and biobased nanocomposites) can and already have helped replacing traditional polymer-placed plastic materials in packaging sector and as edible films, in capsules, for example. For a long time the nano composites lost to polymers due to hydrophilic (dissolution to water) properties of polysaccharides, which limited its uses in food packaging as its own. Some variants have been found with better properties, such as hydroxypropyl methylcellulose (HPMC). Also, nanocomposites of chitosan together with HPMC can improve their properties among other compounds of protein and starch origins. (Arora, 2010)

For example, direct electrospinning manufacturing from dissolved cellulose solution has been under Otsuka's (2017) study. Hardwood pulp with 95% cellulose content and softwood pulp with 96% cellulose content, and intrinsic viscosity of 500 and 1200 respectively were dissolved in mixture of Trifluoroacetic acid and Dichloroethane of several concentrations for several days to create viscous solution. Also, cellulose produced by outer mantles of tunicate, *Halocynthia roretzi*, was tested in spinning. Using metallic electrode plate wrapped in aluminum foil and high voltage in needle, the cellulose solution flowed as electrospun fibers to collection plate foil. The cellulose solutions between 1.3 to 1.6 weight-% gave well-defined fibers and the cellulose was spinnable until 1.9 weight-% after which the viscosity made the electro-spinning impossible. Achieved nanofibres can work as raw material to several fields on nanobiotechnology (Otsuka, 2017)

5 DIGESTER AND USABILITY OF DIGESTER SCREENS

In digester, pre-treated wood chips are cooked in alkalic conditions to separate most of the lignin from cellulosic and hemi cellulosic material. All the wood chips that are converted into pulp goes through the digester to provide sufficient feedstock for oxygen delignification and further bleaching. Digester is fed with impregnated or pre-hydrolysed chips. On top of the digester there is top separator to ensure steady feed into the digester and to provide sufficient mixing and on the bottom of the digester outlet device together with bottom scraper to extract the pulp from digester.

5.1 Process within digester

In the top of the digester is top separator, a large screw (top separator screw) within screen basket separates part of the free liquid (liquor) from wood chips. Slots of the screen keeps chips within the screen basket and lets out most of the liquor. From top separator liquor is extracted and directed back to top circulation and to high-pressure feeder to impregnate chips prior to digester. From top separator chips carry on to first cooking phase or impregnation of the chips. (KnowPulp, 2011) In modern fiberline, liquor is always introduced to chip before digester which improves its reactivity in digester by improving penetration of liquor into the chips. Pre-steaming of wood chips before introduction to liquor has a major effect for penetration of liquor and controllability of wood chip and cooking quality. This can be done around chip meter, or at latest prior to low pressure feeder.

Continuous digesters can be classified to be vapor-phase (steam/liquor-phase) digesters or hydraulic digesters. In vapor-phase digester chip level some gap is left between bottom of top separator screw and chip are pre-heated within digester with hot steam. Steam penetrates the chips efficiently and ensures stable cooking over the movement from top to bottom. In hydraulic digester, chips are directly brought in contact with hot white liquor to start the cooking process.

Depending of wanted output and quality, digester has typically 2-4 screen sections. Within digester, depending of the amount of sections, typically similar amount of major phenomenon occurs. Four stages are pre-steaming at top, cooking and extraction sections in

the middle and wash section on the bottom. Most essential phases that are in digester are cooking and washing stages. Chips are cooked in white liquor to remove lignin initially from woody raw material in sufficient manner. After cooking, extraction of cooking liquor follows. Washing phase in middle or lower part of digester follows the first extraction phase, further removing lignin from pre-treated and cooked pulp. Finally, in lower extraction phase all the liquor possible is removed from pulp mass and pulp is removed through bottom outlet to blow tank. Depending on cooking model and circulations, flow of liquor can be co- or counter current to chips. Chip column constantly moves towards the bottom of digester and they are extracted through the outlet device.

Digester screens have an important role with the functionality and circulations of the digester as liquor is extracted from the digester while chips are moving within digester as chip column is moving down. As described, liquor is extracted and circulated back to earlier (cooking) phases in the upper part of digester to ensure efficient reaction with full liquor (alkali) input and to extend the cooking time with lower alkali charge. Effective area of the screens, together with quality of wood chips directly affects the amount of liquor that can be extracted from digester in each phase and how efficient the cooking is.

5.2 Theory of scaling and typical areas suffering on pulp mill

Scaling in pulp cooking process means inorganic compounds forming a layer on process surfaces, such as digester screens or heat transfer surfaces. It can cause a variety of issues, impacting process or heat transfer, causing unwanted or suboptimal behaviour of equipment within pulp mill. In figure 5 is described generally how scale formation proceeds from cationic and anionic molecules to ion pairs, which form micro-aggregates in the liquid. Microcrystals form micro-aggregates in crystallization that require nucleation centers. Microcrystals are the first particles to gather or absorb to metal surfaces to grow and fuse into macrocrystals, resulting in scaling due to growing bigger with additional scaling ions. In the end, film of organic matter has formed to process surface which can become scale deposit. (Duggirala, 2005)

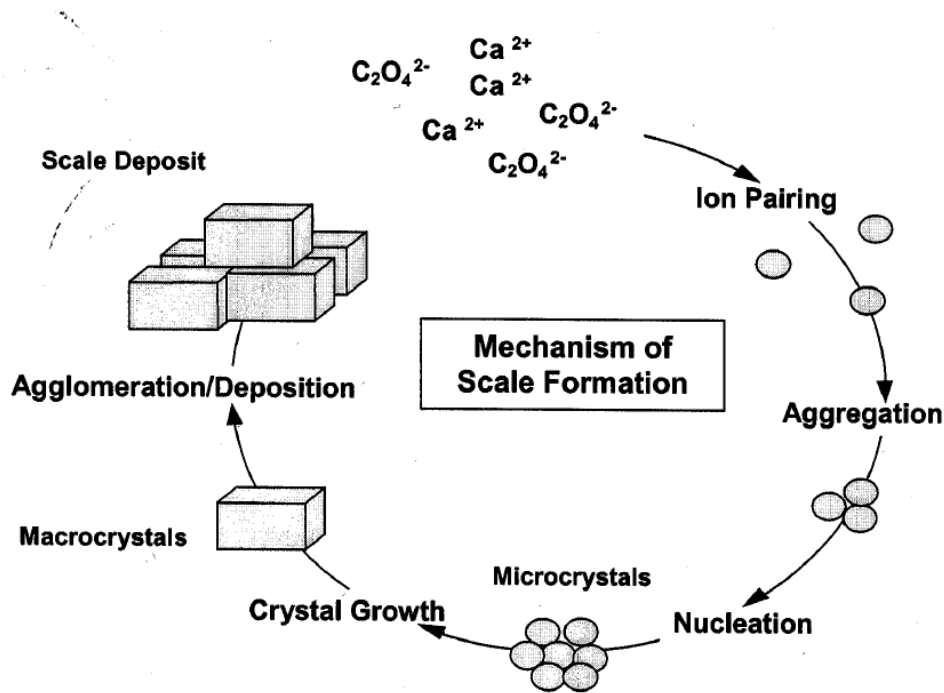


Figure 5. Steps from molecular ion pairing to scale deposit formation (Duggirala, 2005)

5.2.1 Stem of issues with plugging screens and surfaces

There are several potential issues that can result in plugging of the screens on digester. The issues can be separated into mechanical and chemical issues. Mechanical issues are related to the size of chips, design of screens or process conditions within digester that result in mechanical plugging of the screens. Chemical issues are related to reactions that happen in the digester or fiberline that result in creating compounds that are very hard to remove from process surfaces. Many of these reactions can be prevented beforehand with process control or control over raw material fed into the digester.

5.2.2 Calcium carbonate and calcium oxalate

Calcium is the most abundant inorganic element in wood. Based on inorganic analysis made for ash, up to 40-60 % of all inorganic substance in wood is Calcium, followed by magnesium and phosphorous compounds. Hardwood contains even more calcium than softwood, and calcium content of bark is even higher than inner parts of the wood. That is the initial reason why calcium is in the leading role in recognition for lower scaling over the

whole fiberline. (Ester, 1994) Calcium is released from wood during delignification in digester and later washing stages. It can also end up to cooking circulation from fresh water or chemicals. It is an unwanted element in pulping present in black liquor and varies severely between mills. (Li, 2014) The scaling over the shutdown period can be very different, as seen in the figure 6. Formation of calcium scaling is not limited to pulp and paper production, but it also appears for example in oil production and power generation, practically all process piping where favourable compounds for scaling are present. (Chen, 2004)



Figure 6. Scaling can also gather up mass from cooking over time, plugging the screen.

The calcium can come from several inputs within the system, such as woody raw material, process water or re-causticizing, where calcium is present already in white liquor. (Li, 2014) In practice, it is very difficult to limit the amount of calcium coming to process from wood chips. Difference between soluble calcium formed in cooking and when liquor has been used in wood chip pre-treatment should be done. The amount of soluble calcium is low coming directly from cooking process, but it is higher when liquor has been used in chip treatment and the calcium coming from lower temperatures tend to break-up calcium components from earlier stages and cause supersaturation.

Due to solubility decreasing with higher temperature, it is recommended to limit contact between fresh chips and cool black liquor which will increase the amount of soluble calcium in digester and evaporation. CaCO_3 scaling can be the bottom layer of the scaling

phenomenon forming scaling in process surfaces, mixing with other elements. Calcium scaling can be stronger during winter. (Kaila, 1998)

Best methodology to notice the amount of soluble calcium ending up into the digester is to perform elemental analysis for the black liquor by predominance calculation. Controlling the cooking parameters so that soluble calcium does not form insoluble compounds with carbonate is essential to prevent scaling from happening in the first place. (Huber, 2014) Especially modern mills with highly closed circulation, calcium often precipitates in process circulation and once the metastable limit is exceeded, the scaling of process surfaces gets faster if process control methods are not followed or if sufficient elimination of calcium by opening the closed circulation is not performed.

Carbonate in pulp digester circulation needed to produce or form calcite is usually also carry-over from re-causticizing plant, but small part can also be originating from reactions within digester. Portion of carbonate in the digester is reaction product of decarboxylation hemicelluloses producing uronic acids, which is very much applicable in pre-hydrolysis kraft cooking. (Felissia, 2007) Limiting the input from these sources is not easily possible, especially since even the heart wood contains some amounts of calcium. One of the decisive factors when and where the scaling occurs is to control amount of calcium and carbonate, others being the cooking process time, and process parameters such as temperature and pressure. (Huber, 2014)

The most important factor in deciding which inorganic compounds is formed is pH value. Calcium carbonate is typically formed when pH of process is above 9, and calcium oxalate is formed when pH is between 3 and 9. (Ester, 1994) Temperature is also in determining role, as unlike for most of salts, the solubility of calcium carbonate, calcium sulphate and magnesium hydroxide decreases when temperature increases. (Felissia, 2007)

Normally soluble calcium starts causing issues when it reacts with carbonate after reaching its metastable limit, in supersaturated solution containing both calcium and carbonate. (Huber, 2014) Scaling caused by calcium carbonate (or calcite) CaCO_3 results in scaling on process surfaces in digester, such as critical parts of screens as well as bleaching and evaporation surfaces in supporting processes. Calcite can be present in cooking for extended

times without causing any issues, but when temperature or pH swings, it can result in nucleation on a process surface, but only when metastable zone is reached. Metastable zone when nucleation starts is still experimental, but it is considered to be related to high supersaturation levels. (Elfil, 2004)

Calcium oxalate is compound of calcium reacting with oxalate, and it is also an acid naturally occurring in wood. Therefore, limiting its way to digester and cooking flow is also difficult. Monohydrate form of calcium oxalate is the most common in pulping, but di- or trihydrate forms are also possible. Dihydrate calcium oxalate can form in D stages of bleaching, mainly reactions oxalate derived from lignin. That is the obvious reason, together with pH value, that oxalate might not be the main issue causing scaling within the digester. Largest oxalate acid release happens in oxygen delignification and ozone stages, and more oxalate is typically released with ECF than TCF bleaching. Formation of calcium oxalate is result of Oxalate⁻² present in cooking liquor and pH is range of > 3. Oxalate compound formation does not limit only to combining with calcium, but it can form compounds with several metal ions. Oxalate formation can be reduced with enzymatic treatment to degrade the oxalate present in process. Other option has been to add acidic stage that could reduce calcium oxalate issues. (Huber, 2014) The most notable issue related to calcium oxalate is the reactions in over pH value of 3, causing hard to remove compound on bleaching equipment surfaces. (Ester, 1994) Possible treatment for these oxalate scaling issues is acid washing of the equipment or more precisely the process surfaces, if the materials will manage that.

5.2.3 Barium sulphate

Barium sulphate (or Barite) related issues stems from barium ions combining with sulphate ions. In larger scale, barium-related compounds are rarely the largest issue the mill faces. Most of the barium in process is from wood, more commonly from hardwood. Especially high barium content is on bark of the wood, just like for calcium. One specific issue related to barium deposits in wood is, that it tends to co-precipitate with Radon on soil and ends up on pulp mills with wood with barium. Precipitation of these radioactive materials happens in pipelines and wires on site. It is especially likely to dissolve in alkaline stage and then precipitate with sulphate. Sulphate in process originates from pH control substance on

bleaching line or sodium sesquisulphate used in ClO_2 generator. Like calcium oxalate, barium sulphate is less soluble in cold temperatures, so washer temperature drops can cause barium precipitation issues. No high supersaturation is needed for barium to start precipitating. (Huber, 2014)

5.2.4 Calcium and barite within one process and process properties

Calcite deposits occur in temperatures less than 40-50 degrees Celsius, whereas Calcium oxalate and barium sulphate deposits occurs in temperatures higher than that. To limit calcium oxalate and barium sulphate formation is to limit temperature drops. pH variation and regulation are essential parameters to limit scaling, as both use of acid to control pH can increase scaling and reduce it if done correctly. Too high acid load will cause barium to react with sulphate as described above. If sufficient acid load is used and pH is kept typically over 4, fibres on cooking can adsorb barium cations to reduce scaling on surfaces. On the other hand, it is also possible, that while use of acid reduces scaling, it will also damage due to its corrosive nature when chloride gets on steel surfaces. (Huber, 2014) However, usually materials for the process surfaces are on the safe side.

Selection of acid for pH control should also be considered as sodium sesquisulphate can increase the barite scaling by bringing additional sulphate into process. Sulphuric acid should also be avoided in pH control in case barium tends to be the issue with scaling. It is important to control the D_0 -out pH value to keep the scaling as low as possible. Best way to limit the formation of scaling on process surfaces by process control methods is to remove the calcium ions and barium ions, as well as carbonate, sulphate and oxalate from cooking flow or stop them from entering the digester in the first place to highest economic extend. (Huber, 2014)

5.3 Impact of scaling on process

Scaling on pulp mill will result in different kind of issues depending of the stage the scaling occurs. As described above, the type of scaling has strong correlation with the dominant temperature and pH value and variance of these within the process and process phase in question, as well as saturation level of organic matter.

5.3.1 In digester

Digester temperatures are typically high in comparison with other process stages within mill. This means process surfaces are susceptible especially to calcium carbonate supersaturation, which occurs more in highly base pH and temperatures of over 50 degrees, on a non-linear line. In general, the lower the pH, the lower temperatures are required for calcite scaling to start forming. (Huber, 2014) This means any big variation on digester temperatures and pH swings (temperature and pH shocks) will result on supersaturation to begin scaling on process surfaces. Also, the dipping of pH coming from acidic conditions of pre-hydrolysis (pH 3-4) to (base) alkaline conditions of the digester should be affected by rising pH early on digester vessel and to reduce the sudden pH shock in the process.

The most severe issue that scaling causes in digester is the scaling occurring on critical process surfaces. Especially screens, which work as sort of a filter for cooking or more precisely black liquor extraction during the chip cooking, scaling can affect the open areas of screens and lower amount of extraction done through them to optimize liquor to wood ratio and process control of cooking. Being unable to extract black liquor over the wanted areas of the digester will also lower the NaOH charge, which will lead to insufficient cooking and increase the chemical charge demand in later stages of the delignification and bleaching. Part of the liquor extraction is also done from the bottom of the digester to reach desired percentage of solids on pulp mass, so further treatment can be performed on optimal equipment capacity and as little additional energy, water, or chemicals as possible.

5.3.2 In heat exchangers and power boilers

In the same manner, scaling in heat exchangers and boilers occurs. Scaling in boilers results fouling of piping which decreases heat transfer over the heat transfer surfaces and increases heat transfer surface temperatures. Mechanical cleaning systems are implemented more easily on boilers, which must be equipped with soot blowers because fouling caused by ash is often a constant phenomenon on the piping circulating on heat exchanger pipe surfaces. Ash carry-over in flue gases is the main reason for outer surface fouling, even when process control is done correctly. Within the hot water pipes, in addition with previously discussed CaCO_3 and $\text{Mg}(\text{OH})_2$, inner scaling is often caused by silicon dioxide (or silica) SiO_2 , which

is unwanted substance is boiler water, naturally occurring in take-in waters to the mill. (Luo, 2012)

Outer fouling of heat transfer surfaces on high boiler temperatures can cause quick damage, if left untreated, such as slagging on furnace walls and heating surfaces, and lead to corrosion of internal surfaces of the boiler over time leading to mechanical failure. Both mechanical (soot blowing, pulse detonation) and chemical (addition of chemicals to reduce formation of scaling compounds) means are used to reduce and neglect the negative effects of fouling. (Junaid, 2017)

Mass volumes in comparison to pulp mass flow are smaller, so process control is reasonable, but also essential to maximise the lifetime and safety of boiler piping. The boiler water plants are equipped with several purification stages, with mechanical, chemical water cleaning stages, but if silicates end up in boiler and further steam stages, it can rapidly colloid with other compounds resulting local damage to the piping. From the boiler, the potential fouling component will carry on to the steam turbine, in which any excess compounds may cause damage of high-pressure turbine stages and scaling on the rotors.

5.3.3 In evaporation plant

In evaporation, water from black liquor, which has been used in cooking, is evaporated with multi-stage evaporation units to increase the efficiency of burning it in recovery boiler. The dry solids content of black liquor increases as water is evaporated, and at the same time evaporation plant is typically the most steam consuming part of pulp mill. Typical issues within evaporation scaling-wise are crystallization of double salts of Na_2SO_4 and Na_2CO_3 . Sodium salts are not very hard to remove and can be performed while plant is running. Still, since the phenomenon of salts crystallizing on metastable limit is a known and metastable limit is very difficult to define, possibly due to several chemical compounds present in the process and modelling of fouling rate in evaporators is not possible. (Karlsson, 2013) (Kaila, 1998) This might also indicate that since scaling in digesters is also dependant of this metastable limit that must be exceed for the scaling to start, receiving conclusive evidence of digester screens usability would difficult other than experimental means.

5.4 Scale formation types

Especially calcium carbonate scaling has persisted in pulp and paper industry, as well as several other field of process industries for extended period, but studies related to these issues have been resolved more on lab study level, rather than being performed on actual mill scale level. Two main types of scaling, bulk precipitation and surface scaling, vary in formation speed and variance in process conditions. In Chen's study from 2005, it was shown that bulk precipitation, which means formation of colloidal "bulks" on intermediate liquid, only becomes an issue when supersaturation stage of Calcium is achieved. On saturated and sub-saturated stage, formation of bulk precipitation is relatively small. (Chen, 2005)

Surface scaling occurs when calcium and carbonate is present on liquid. Surface scaling means actual scaling formed on metal surface within the test vessel, first in nucleation stage and late growth stage. No supersaturation is needed in order to surface scaling to form and gather on (metal) process surfaces, but the reactions greatly accelerates when saturation is higher. It was also noted that practically no formation of bulk precipitation happened before saturated stage was achieved. (Chen, 2005)

5.5 Prevention and post treatment of scaling

Prevention of scaling more economic than removing the scaling when it has already happened. In figure 7 has been classified the preventive and reactive methods for actions against scaling. Prevention strategies include process control methods, such as process flow quality inspections and process circulation inspections, chemical process simulations (in collaboration with regular process simulation), and mechanical or chemical removal of scaling-boosting compounds from cooking. Post treatment methods are limited to removal of scaling from surfaces with mechanical and/or chemical treatment after the incident of scaling has already occurred. Using post treatment methods often result in or demand process shut downs or cause other limitation to production due to process surfaces being inaccessible during normal operation.

The post treatment methods often require stoppage of production to access the critical process surfaces, resulting losses to production and active working hours from maintenance personnel. Even brief shutdowns for process critical equipment such as digester can cause major economic losses when unplanned shutdown takes place taking into account huge volumes during normal operation and required work force for the maintenance. The actual applied methods on mill site should include one or several of these to ensure sufficient control of scaling phenomenon on digester and neglect or minimize negative effects.

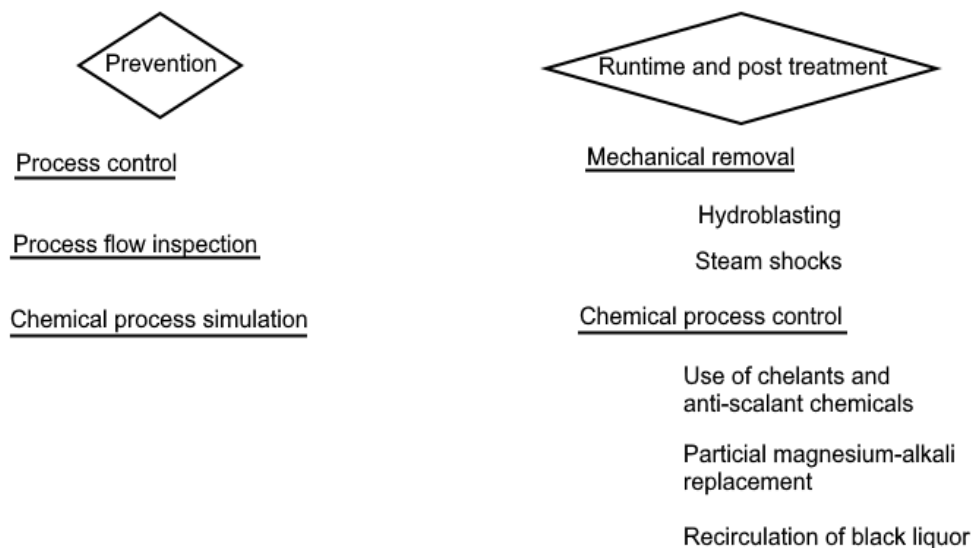


Figure 7. Classification of common potential reactions to impact scaling effects

5.5.1 Prevention strategies

Prevention strategies include both theoretical and actual process control means to either prevent the beginning of the process of scaling by not letting the nucleus formation to begin. Recirculation of black liquor allows more the for the chelants to improve anti-scalant chemical's efficiency by improving the reaction rate. All of the chelants cannot react during one run through the digester and part of chemical is lost in black liquor. The recirculation method impacts the scaling by removing metal ions from circulation by redirecting part of black liquor into evaporation. pH plays a role in this, because controlling of pH to make the environment unsuitable for compound formation. Another option is also making sure all or at least most of potential chemical sources are minimized so that the compounds won't end

up in digester or bleaching in the first place. This can be difficult, because as discussed previously, some of the compounds, such as the CaCO_3 , are only formed within the process due to chemical reactions, so limitation of these can be difficult or even impossible. The topic of this thesis also mainly falls under this prevention method category, as the coating does not impact on the inputs of the process. It only protects critical areas by making the nucleation platform unfavourable to start on this area.

5.6 Runtime and post treatment

Runtime and post treatment methods can be applied when it is already clear that scaling is or has occurred in the vessel. These are more precise and often reactive methods to minimize the issues caused by the phenomenon.

5.6.1 Mechanical removal

Mechanical removal is a direct mean to remove the hard-to-remove surface scaling formed on the process surfaces. Washing of the surfaces is possible to do with either acid compounds or chelates as removal agent together with mechanical means, that include hydro blasting the process surfaces and use of steam shocks. (Huber, 2014) Mechanical washing is the last resort when talking about scaling treatment as it always requires shutdown of digester and binds manual labour. Mechanical washing should only be prioritized when scaling influences the critical surfaces, or when natural maintenance shutdown is scheduled, and digester is maintained in other ways as well. The worst situation possible is that the process has to be stopped due to the scaled surfaces or that surfaces are damaged due to scaling.

The modern trend of lengthening the interval between shutdowns to up to 1,5 or even 2 years makes it even more essential to be able to control the scale formation within process surfaces before they occur, as scaling over two years could easily result in unnecessary shutdowns, especially when time is getting closer to the scheduled maintenance shutdown. It is also known that the mill would be taking considerable risk running with plugged surfaces. Some mills in the past have had to stop once every ten or so weeks to clean digester from scaling. (Greer, 1999) The process control methods have improved significantly over the last twenty years, but the topic is constantly on the table when mills attempt to prolong the shutdown

sequence. Process control can and should be done constantly or rather automatically during to runtime to minimize the scaling over time and rather than reacting to existing issues, and potentially add anti-scalants when needed.

5.6.2 Chemical process control

It is possible to prevent scaling with anti-scalant chemicals in cooking prior to scaling occurrence. These chemicals however are often costly in comparison to process-based methods. Most common anti-scalant agents with longer history in industry used are phosphates and phosphonates. Newer chemicals used are polyphosphates, like polyacrylic acid and polymaleic acid. Anti-scalants include chelants, organic dispersants and man-made polymeric anti-scalants. Anti-scalants are usually wanted to get rid of due to the high price and environmental point of view. (Huber, 2014)

According to Duggirala, 2005, anti-scalants uses one of three mechanisms to stop scaling and nucleation formation

- Threshold inhibition
- Crystal dispersion
- Crystal modification

Chelants are compounds that bind metal ions in solution so that they cannot react further to unwanted compounds to cause process issues, such calcium and barium. (Huber, 2014) Use of chelating agents (or chelates) is not always popular due to cost impact and high consumption per tonne of pulp. Stream volumes on pulp mill are high and chelating agents only bind certain amount of metal ions, which means the use of chelates must be continuous if metals end up in closed circulation. It is worth noticing that most popular chelates used in pulp industry are not bio-degradable, so they also add load on wastewater plant and increase oxygen demand of waste water treatment. Some environmentally friendly options has been developed for EDTA, ethylenediaminetetraacetic, such as S,S'-EDDS, S,S'-ethylenediamine disuccinic acid, with fairly good results of lower environmental impact and high processing value. It is likely that popularity of biodegradable chelants will increase in

the future to reduce impact to environment and lower oxygen demand within mill. (Jones, 2002)

Study of Felissia, 2007, showed that Calcium will precipitate in cooking liquor until temperature of liquor was increased to 135 °C. Then supersaturation reduced the direct amount of Calcium ions, by precipitating part of Ca into CaCO₃. Use of only DTPMPA diethylenetriamine penta (methylene phosphonic acid) reduced the content of calcium of pulp by approximately 22 % of the control level (in comparison to pulp without any chelant use). Use of both polymers and chelants together improved the calcium extraction without weakening the yield or viscosity of pulp. (Felissia, 2007)

5.6.3 Mechanical process control

To limit calcium carbonate crystal growth and to eliminate calcium scaling in evaporation, patented calcium deactivation system has been developed. System is formed by direct contact heaters in series with reactor tank that provides residence time for calcium compound break up and to avoid formation of crystals in liquor. This deactivation method has been applied in mills with scaling issues in evaporation plants and the case studies indicate that the situation has been improved afterwards. (Kaila, 1998)

5.6.4 Other studied methods

Magnesium-based alkalis might provide alternative solution to Sodium-containing alkalis such as most popular NaOH. Even replacing part of Na with Mg, and even if 30% of used NaOH is replaced with magnesium hydroxide, Mg(OH)₂, on molar basis, it is possible to reduce scaling caused by calcium oxalate. Mg(OH)₂ is currently twice the price in comparison to NaOH, but lower scaling issues can compensate this cost, especially if only part of NaOH is replaced and alkali costs are not doubled. Presence of magnesium in process also inhibits the calcite formation, therefore reducing hard scaling in process surfaces. (Huber, 2014)

Some studies have been made also in regular paper-grade kraft cooking about the scaling. Calcium carbonate scaling often occurs in process surfaces also before digester. With small

recirculation of black liquor back to chip circulation it was possible to stop the scaling and remove already scaled substance from process surfaces in early process stages. This is most likely result of chelants binding metals only in stoichiometric amounts, so when chelant flows through the process once, some unreacted chemical is left to black liquor. (Banerjee, 2002) This also improves the chemical costs in comparison if unreacted chelants would go directly to wastewater treatment. It might a topic of further study if same method could be applied in pre-hydrolysis kraft cooking by circulating small portion of black liquor back to the pulp leaving the pre-hydrolysis vessel or even lower part of pre-hydrolysis vessel, as long as it is possible to do without messing up the chemical balance. Some studies have also been performed with ultraviolet treatment of process solutions and it has been noted to be effective method to limit the crystal growth rate by around 85% therefore limiting the scaling of the process surfaces, in this case studied membranes surfaces. (Chanbasha, 2020)

5.7 Coating of digester screens

Coating means a treatment of screen surfaces by protective layer of material in the screens. The material must have protective attributes and capability of limiting or removing the issues currently being faced in the process. In general, the meaning of coating of items in general is to protect critical surfaces and should not be applied over the whole equipment or process surfaces. Typically, this is also not an economic approach. The main target is to reduce the requirement of maintenance, here extraction of compounds from screen surfaces or acid washing of the digester and to extend the usability and lifetime of the screens by impacting the costs and downtime caused by the issues. Naturally, coating of critical surfaces has little to no effect on the scaling occurring on other surfaces that are not coated, and the scaling can still cause issues on other areas.

The basic idea of the experimental part would be to find out if there are applicable surface coating materials to keep the scaling out of critical parts of the digester. Within a typical pulp digester, as described in earlier chapter, exists a hot (up to 150-170 °C depending on section), base (pH value 10-13.5) and pressurized (3-5 bars) atmosphere with the screens constantly being in contact with liquor and wood chips, whereas the pre hydrolysis stage is normally on very low pH range so highly acidic. This creates high demands for the applied

coating material on mechanical durability but also chemical properties that the coating material must tolerate for long periods of time. Minimum target of the durability of coating material should be the maintenance shutdown interval, typically between one to two years.

5.8 Polytetrafluorethylene

Polytetrafluorethylene (PTFE) or Teflon has been used in several industrial and home applications for decades. Home applications include cooking pan coatings for non-sticking surface and industrial applications include sealings, slide bearings, membrane filters and insulation tapes for several fields. On pulp and paper industry, PTFE coatings has been used at least for press rolls to have non-sticking surface against pulp, lower the corrosion rate against process water and chemicals, and improve availability of equipment in co-operation of these two functions. (Timperi, 2015)

5.8.1 Features for PTFE coating

The most important features for this application in digester use, that PTFE has, are very low friction factor, fair toughness, and high abrasion resistance. PTFE is highly non-reactive and durable in the presence of most chemicals, and it can be applied to surfaces, modified on its own and it is non-toxic on its solid form. Technique for PTFE coating is also well known, as the coating is done directly with powder or spraying on wanted surface. Other option is to heat the PTFE over the melting point and apply it in gel-like substance on to the surface, after which the item is cooled so that creeping is minimized. One existing application is also PTFE films, that could be valid option for rebuilding the coating during shutdowns. Creeping might be a valid issue considering that the PTFE is on vertical surface with constant flow against it and over time. All in all, a wanted coated surface must be solid in terms of coated area, and it has to endure the process conditions, both mechanical and chemical. Some other notes about the properties are made in the following chapters.

For the PTFE coating the items must be warmed up to over 300 °C, which requires special equipment for heating the screens. A study related to drying machine roll coatings has also shown that the wearing resistance for PTFE's is quite low, but it can be improved by applying a prior bond coat between the metal surface and PTFE surface. (Timperi, 2012)

5.8.2 Potential chemical issues of PTFE coating

Another issue that such coating material might face in pulp application is the tendency of carbon-fluorine bonds react with metal ions, such as Ca, Na and Mg actively. This Calcium bonding and chemical reactions is exactly what is being treated with in this experiment. It could, however, also turn into a positive effect if it is shown that the surfaces can extract metal ions from pulp flow and the compounds generated can be removed from flow effectively or treated otherwise if they are bound on the screen surfaces. Continuation study topic could be the extraction of these adsorbed metal ions for screen surfaces in case they become an issue.

5.8.3 Potential mechanical issues of PTFE coating

The screen surfaces will face a strong wearing within the process. Wearing can be classified to be either adhesive, abrasive or erosion wearing. In digester conditions, being in contact with not only chemicals but also with wood chips and unwanted material particles that end up in the digester can increase or cause the wearing. The most notable of these three is still erosion, which is the local wearing, even while PTFE has high tribological features, most importantly low friction factor, external force with harder substances, such as sand, rock and metal particles will cause erosion to the surfaces. It is not unusual that these particles end up in digester, although several substance removal equipment are included in the feed line, such as sand separators, tramp material separators and relief strainers.

This might turn out to be a critical issue because PTFE coating is soft in comparison with metals and some soil compounds. It is a known fact by practical experience that some unwanted substances do end up into the digester no matter how careful and multistage removal process is used. Especially if a larger, sharp metal objects were to scratch the surface of PTFE-coated screens constantly, it would obviously make holes or scratch openings in coating surface. This might in turn expose the screens for regular scaling phenomenon with increased tendency for scaling in sticking surface due to the potential grooves on screen plates. It has been noticed that adhering of fouling particles is faster in imperfections in the surface, such as grooves and gaps. However, direct relationship between surface roughness of stainless steel and adhesion of fouling has not been shown on Calcium carbonate reference

case, or at least there is no linearity between them. (Liu, 2011) It is possible that larger grooves might turn out to be bigger issue.

Temperature related issues are a part of the necessary maintenance concept of digester screens. PTFE's transformation begins in temperatures in the melting point of 342 °C, and reactions even lower than that with presence of metal compounds. During the potential repair of screen structures, it is not unusual that screen supports are welded while screens are still in place. In order to ensure the solid coating after repair works, screens must be kept under these critical temperatures.

Mechanical stress-wise, the screens themselves are quite robust and supported to digester structures or walls. Therefore, it is unlikely that screen coatings would suffer from breaks or holes due to yielding stress which would require expansion and subtraction of the screens while being in place within the digester.

5.8.4 Manufacturing of PTFE coated screens

One of the major issues related the actual production of the screen coating is that it cannot be welded on the screen, which would improve the repairability of the screens during maintenance shutdown. PTFE is not a thermoplastic, so welding repairs is not an option. Injection moulding, where material is first plasticized, then sprayed and cooled in the end might be the best applicable method, because of the mobility and possibility to perform on site or at workshop conditions. Even repairs on maintenance shutdown would be an option, if the mobility of equipment is possible, and screens can be intact within digester.

It also possible to apply primary surface coating below the PTFE surface to improve the wearing and abrasion resistance against the conditions in the process. Hard-coating surface materials can be Wolfram carbide or ceramic material, however with improved wearing resistance, and hardness. Wolfram carbide can be mixed with metals such as Cobalt and Chrome to improve durability and hardness as necessary. To improve corrosion resistance, it would be possible to use mixes of Wolfram-Carbide-Nickel or Titanium-Carbide-Cobalt, or ceramic primary coatings, such as Silicon carbide or even Silicon nitride which provide very high hardness, but silicon-based coatings are also more expensive to use. (Timperi,

2015) In terms of digester use, improved hardness does not have to be in the level of wearing sleeves for example, as the primary use is to provide higher lifetime for the screens, but rather to improve the smoothness and sliding capabilities of the surface will be improved. It can also improve chemical resistance, but it should not be as critical in terms of alkaline conditions in the digester, as mechanical wearing resistance should be prioritized.

5.9 Study for scaling occurring in uncoated and coated screens

To benchmark the effectiveness of the coated screen, a comparing test run should be organized. Since the materials for the test run could not be organized in time, the study shall be made as literature work. First potential test run setup is described to extend possible. Chemicals used and present in the run are discussed, and variables within the test run scope and potential issues with the test run parameters are presented. In the end, the potential results are estimated and the terms in which the coating of the screens can be beneficial to mill are explained. Evaluation of the test run is estimated in the terms of screens properties either being better by not having scaled, scaling removability and other key parameters which would give them an advantage over the traditional non-coated screens.

5.9.1 Test run

In the planned test run screens were to be placed into cooking liquor received from dissolving pulp mill. The cooking test is performed so that the cooking liquor circulates through both of screens with equal flow (through the screens), temperatures, and pressure. The liquor used in the benchmarking should be received from a place where scaling occurs in real life, like hot black liquor tank of displacement batch cooking process, which is the liquor used in the first (cooking) stage of batch cook after black and white liquor neutralization. That way the chemical balance and composition is as close to real life situation or as close to normal cooking liquor as practically possible.

A desired reaction during the cooking test would be scaling on the screens which can be analysed in terms of thickness, size, and removability. The test runs can be performed so that first run is done on lower end of test temperature scale, for example at 100 °C for 20 minutes, after which the screens are inspected. The temperature is increased as many times as desired scaling level is reached, on the interval of 5-10 °C per test. The chemical reactions of CaCO_3 are practical to aid to performance of the tests, as the solubility lowers when temperature increases as discussed in the theory chapters. In the following sections, the original, non-coated screen is referred as 'reference screen' and the coated screen as 'test screen'. Therefore, the test should be organized so that temperature is increased in consecutive test runs as many times as required until the wanted scaling phenomenon has happened on the

reference screen. After that the test screen can be evaluated to be either better, worse, or equal to the reference.

5.9.2 Chemicals

Chemicals used in the test run should be received from mill, which produces dissolving pulp with batch cooking process. Issues with resolving test run chemicals is mostly related to CaCO_3 and its solubility. The basic form of CaCO_3 is solid in the room temperature. Therefore, it must be dissolved into the cooking liquor by chemical reaction in separate chemical compositions. This can be done with help of existing studies related to CaCO_3 solubility tests.

To create a supersaturated calcium carbonate solution, a test from Khormali, where scaling was inspected in oil wells could be adapted to inspect the scaling phenomenon in pulp cooking as well. One option to create the supersaturated calcium carbonate aqueous solution can be adapted from the drilling-based oil well test, formed from incompatible mixing of injected water (water to maintain the pressure during oil pumping, in respect of calcium chloride) with formation water (also known as field water, which exists in rock and contains a lot of salts, such as calcium, sodium, magnesium, and potassium ions as well as some carbonates and sulphate compounds). (Khormali, 2014) In Chanbasha's study, a combination of sodium chloride and sodium bicarbonate were applied to study CaCO_3 properties. Chanbasha's study was applied in water-based solution. (Chanbasha, 2020) In terms of test run, if the scaling agent used in the test run is same as in pulp cooking, the indication of the results should be trustworthy. Naturally surrounding chemical balance will have an impact on the effects in the long run.

The precipitation of the salt in this solution occurs only under supersaturation of calcium ions within the mixture and it can be achieved by removing or decreasing dissolved CO_2 , increasing the temperature and lowering pressure. The reduction leads to precipitation of excess amount of carbonate in the production vessel and formation of CaCO_3 . The objective of the Khormali's study was to investigate calcium carbonate precipitation in formation waters by varying temperature and pressure and to study the effectiveness of inhibitors typically used in the field of industry of oil and gas production. (Khormali, 2014)

Calcium carbonate is solid on room temperatures, and its solubility to water is very low. To reach the desired supersaturated state, the removal of dissolved CO_2 in the water solution results in precipitation of CaCO_3 from saturated media (by salt forming ions) and process is even stronger when pressure is reduced below saturation pressure. (Khormali, 2014)

As discussed earlier, CaCO_3 solubility reduces when temperature increases, and therefore stronger reaction with deposition can be seen if temperature rises. Also, pH value of the media will influence the amount of CO_3^{2-} present in the solution and impacts indirectly the amount of CaCO_3 in the solution by limiting or increasing the available carbonate ions in the solution. In this case, acidic conditions will have much higher solubility in comparison to media with alkaline conditions. This, in turn can help to explain why the supersaturation (and precipitation followed) will occur in pulping process with swings from acidic to alkaline condition due to alkaline conditions decreases solubility of the calcite in the media. The presence of other ions, such as Na_2CO_3 will also impact the solubility of CaCO_3 with more ions in the water the CaCO_3 solubility lowering even more. The pressure drop will also allow the scale preposition to start even at lower temperatures. All these conditions can improve the chance of starting the reaction. (Duggirala, 2015)

The biggest issue of dissolving CaCO_3 to liquor is that it does not dissolve well in base solutions. CaCO_3 will better dissolve in acid, as it reacts with hydrogen ions forming calcium ions, carbon dioxide and water. It will however dissolve to water with carbon dioxide forming calcium ions and hydrogen carbonate. Mixing acid with black liquor is not a valid option since it forms hydrogen sulphide H_2S , which is a combustible gas and toxic to humans due to its effects on cellular respiration.

5.9.3 Variables

The limitation of the test runs and comparison to mill environment should also be noted. Some differences between the screen plates can and in real life will occur, as no two screens are identical. The variance can occur in the following screen parameters between the test screens and their effects should be noted. Surface roughness, material, screen slot size, screen slot angle towards the flow and surface finishing that may vary between the screens. It is obvious that the coating reduces surface roughness, although in reference studies no

major difference between polished or unpolished screens have been noticed, meaning that surface roughness has little impact on the scaling. Too low of a flow speed through the screen can speed up the scaling process so realistic circulation speed and flow through the screen is essential to reach realistic results.

Regarding the surface roughness, eliminating scratches is more important than lowering the screen surface roughness per se. Material of coating also has an impact on the lifetime of the screen, easiness of installation and coating quality and manufacturing of the screens. The slot angle means the angle between the vertical screen surface and the slot is made so that the screen allows particles to pass through if the fiber gets on the slot, but the fibers will not get stuck and plug the screens. Other notable parameters can be the general dimensions of the screen, as the thickness of the screen can affect the length of the slots (or channels) which affects the flow restriction and pressure difference over the screen by a small fraction.

5.9.4 **Other open issues with the test run**

Other issues are related to test chemicals and digester used in the test. In this case the used test chemical is black liquor, which already includes large quantities of dissolved compounds of lignin, and small amounts of hemicelluloses and other extractives from wood, so there is no need to use wood chips in the test run, if chemical balance is realistic and the formation of scaling can start. Not using wood chips in the test run can also help to control the chemical balance and flow through the screen since all the chemical reactions have happened prior to test run and media in the digester is homogeneous. Using wood chips could however add Calcium to process, which in turn could help the formation of CaCO_3 within the test vessel.

Setting up the screens inside the digester can be done in various ways. For example, by installing them either in basket within the digester or hanging or welding the screens inside. Key point is to have liquor flow through the screens to inspect the critical surfaces and flow speed through the slots as close to normal digester operation as possible. Naturally, to get the best reference test, the surface quality and parameters of the screens must be as close to each other as possible. It would make sense that smoother screen surface has lower tendency of scaling to being with since the minor scratches on the surface can exist if the screens are not polished or coated with smooth surface coating, although as mentioned previously,

reference studies has noted that it has minor impact on the surface scaling. So as long as the difference is not significant, the difference in surface quality should be affecting the outcome in large margin.

The liquor should also be analysed prior to test run to make sure the composition with which the test has been done and that has led to scaling is known for reference. This should either be done in laboratory of the mill or with the laboratory that is performing the study. It should be made sure that the supersaturation level can be achieved in the liquor, and the scaling is possible to happen. The supersaturation must be achieved exactly with wanted chemical, CaCO_3 , as other salts such as Na will have an impact on total level of CaCO_3 soluble and will supersaturate in similar manner with lower amounts present.

5.10 Evaluation of the potential results

As the test run was not possible to perform in given time schedule, the estimate of the results is presented. The wanted outcome of the test run would be to have scaling occur on either both screens or at least one of the screens. This would indicate that the supersaturation of CaCO_3 has been achieved and reaction has started successfully. If the test run is successful, two main scenarios can be noted. First option would be that the scaling has occurred in the reference screen that has not been coated and the other is clean or with limited scaling appearing on the screen. The other main option would be that both screens would have the scaling occurring.

In case both of the screens have scaling formed of them, a comparison should focus on the actual properties of the screen scaling, in terms discussed above, including ease of removal of scaling on the screens, type of the scaling, including parameters such as thickness of the scaling layer formed on the screen and the total area of the scaling formed on critical surface and its location on the screen. If scaling is happening in the wall side (outer side of the screens), it can be difficult to remove without hinges on the screens and can affect flow by restricting it and changing the circulation balances. If the scaling is limiting the flow in comparison to reference screen, then the effect of the screens coating could be deemed to not assist with the issue at hand, in case the removability is not notable better.

However, keeping the scaling from forming on these critical surfaces can help the operability of the digester between shutdowns as discussed. Effective methods that mill can apply to prevent scaling and deal with formed scaling surfaces are presented in the chapter 5.5. So even if the screens are coated to further ensure that the digester stays in operating condition, chemical or process control should be applied. Even if screens are treated, there should be a method to control chemicals in the how to remove compounds from cooking flow, such as chelants or other anti scalant substances. Although closed circulation will provide a major benefit over the older, open loop chemical circulations in terms of chemical savings, opening the system with partial extraction of black liquor and recirculation of hydrolysate to maximise the efficiency of scaling control and limiting potential scaling formation, leading to savings in maintenance times and unplanned shutdowns.

5.11 Profitability and limitations

When a suitable material for surface coatings is found, the screens should be protected on constant basis. During normal shutdown maintenance, the condition of the screens and coating should be inspected carefully to ensure the condition of coating. In case the coating has been damaged a new layer could be applied to continue the improved performance of the screens. To further improve lifetime of the coating, hard coating of the screens could be applied. When new screens are being installed, screens can be coated already during manufacturing or at latest when screens are installed at the mill. To confirm the efficiency of the coating and its effects on the non-sticking area within the digester a larger plant scale study should be organized to give full confirmation.

The comparison of the benefits found in the study should be evaluated by comparing to negative impacts of scaling. It could be compared to potential unplanned shutdown or over a specific period of time, for example two years. To get the realistic cost evaluation, all costs related to losses due to plugged or scaled screens should be considered. These include the workforce of washing, equipment used, auxiliaries of the washing, such as scaffoldings, water consumption and chemical consumption. If the digester works are delayed due to washing and they lengthen the shutdown duration or if the shutdown due to screen issues is unplanned, the lost production could also be considered on this evaluation.

Although it is recommended to keep using chelants and anti-scalants as long as the scaling occurs on the mill and even if the screens are coated and effectively protected by the surface coating, the chemical consumption could be taken down which leads to savings and positive environmental impact in the long run. Partial recirculation of the black liquor could also be applied in the process which improves the reaction level of chelants.

It should be noted that coating of the screens is one of many factors impacting the availability of the mill and digester. Best outcome is always reached by combining process control and chemical methods to avoid scaling. In addition to these traditional methods, coating can provide a new tool to further ensure smooth operation of the digester, but most likely it alone cannot solve the issues of the mill is facing with scaling issues. Even when coating is applied to screens, the scaling issues will be likely faced on other parts of the mill which can have similar, shutdown resulting impact.

5.12 Relevant studies

As the performance is the study regarding the coating was not possible to perform, the first and most economical way of testing in laboratory was described in the test run chapter. It will give a good indication if the coating has impact of the assumed calcium carbonate scaling. After performing that initial study, the mill scale study will be performed to test screens in real life situation. Naturally the mill study will be more realistic, since in laboratory all chemicals are treated separately, but in the mill the screens are exposed to several damage-inducing factors, such as mechanical stress and chemicals.

In order to give conclusive estimate of the effectiveness of coating as a method to avoid scaling on critical surfaces, it would be beneficial to perform the test runs on different processes, such as batch and continuous digesters, with pre-hydrolysis based on water and acid processes, as well as different process stages. All the scaling on pulp mill is not the same, and salts on process vary drastically based on the wood species and related functions, such as age of the mill and upgrades performed on the different parts of the mill. As mentioned in earlier chapters, calcium can end up the digester from re-causticizing plant, which can indicate issues on the chemical balance. Other compounds can end up the digester

from insufficient barking. The whole wood and chemical balance should be considered when resolving the scaling issues, which would be a potential study topic.

Further estimation could also be done in the economic aspect of the coating technology, ROI time and impacts on the mill. Naturally the coating will increase the maintenance costs, but it can pay itself back several times in terms of improved availability, lower maintenance due to lower scaling rate and manpower costs. A mill scale study could also shed light on the topic and give realistic figures on the potential savings and ROI time in realistic real world case. Ideally modern mills want to plan shutdowns and maintenance schedules further and further to the future and minimize unplanned down time of the mill, which leads to lower down time in production and brings savings to the mill. Run-to-failure maintenance culture does not function in modern process technology and it can lower the production by unplanned shutdowns and interferences in both output and quality of the pulp.

6 CONCLUSION

All in all, based on the literature and studies read to shed light on the topic of scaling, scaling control and methods can improve the operability and availability of the mill. It is safe to assume that overall savings and benefits that can be achieved by following a routine avoiding scaling can save a lot of work, improve the lifespan of digester, save environment, and bring savings to the mill. One method, such as using chelants or limiting the temperature swings, alone is not typically sufficient, so to limit the scaling, overall process control and chemical balance control over the whole mill is worth studying to get rid of the scaling issues when they occur.

6.1 Scope of work

The study concept was planned through but due to delays on the schedule the test runs were not possible to perform. The test run would have been first of the series that would have finished on the real-life test on dissolving pulp mill or any mill having scaling issues on the digester screens. Scope of studied topic was approached by considering open issues in the potential test run and shedding light on the theory behind phenomenon. The thesis first described the dissolving pulp process, development of the future in dissolving production, and in the practical part gave good basis and raised several important factors which all attribute to the availability of the digester and how to control the scaling forming inside digester vessel. The scaling phenomenon was the opened and potential trouble sources were named. The analysis of the potential effects coating of the screens could have been evaluated based on the existing studies from materials in similar studies and they have been combined to theory of scaling in order to give extensive description of effects coating can have to digester together with total process control, chemical balance knowledge and other key parameters. However, the test run could have given new perspective or opened new further questions regarding the issue the real-life mills are having with their process.

The real-life situation where scaling issues are being faced on the mills even during the writing of this thesis. Many large pulp mills, manufacturing kraft or dissolving pulp are facing scaling issues on the digester screens even today, so to troubleshooting process issues

case-by-case can be very time consuming. The solution typically also requires highly experienced equipment and process specialists together with complete analysis of the process to solve potential issues. The solution of coating the screens does not take out the full effect the scaling is resulting at mills, but it would be very straight forward reaction. If the scaling could be kept off the critical surfaces even during normal operation, it would give more time for the mills to react and modify the process so that scaling does not form as strongly. This will also lead to savings as downtime for modern pulp mills can be very costly due to high production volumes. Although the consulting of experts can give guidance on how to avoid the conditions for scaling to begin, it would be favourable on grass root level that some actual mechanical or lasting chemical changes to process would be made to implement the solution on the mill process.

6.2 Discussion

The evaluation based on the thesis is that combining several process control methods and being aware of chemical balance can help controlling the scaling formed on the digester. It is normal and very likely that chemicals that can start scaling formation will end up in the digester at some point of the long-life cycle. Therefore, acknowledging the risk factors that scaling will cause issues in the digester and methods to limit them will help the mill prepare for the dilemma.

Although the test run was not possible, and similar type of coating of screens has not been applied in similar uses, it can be said that applying new method of coating to limit scaling-limited issues can be a new tool in helping the mill to prevent scaling, together with other methods. Being aware of chemicals in the cooking such as calcium from woodyard with wood chips, carbonate from re-causticizing, as well as chip quality and chemicals coming from wood yard and chip feed will give the elements for the operator to control and react in case issues start to come up. Other essential elements include other metals present in the cooking stages, as they can also scale with carbonate. Regardless of the age of the mill and digester, it is continuous work as quality of chemicals and wood chips can vary over time.

Based on the studied literature, use of chelants can be recommended even if the scaling is not an everyday issue, as it provides security on the screen so that the surfaces stay clean and extract harmful components from circulation over time. It is also worth noting that post reactive use of chelants and anti-scalants is not always efficient due stoichiometric nature of chelants, so chelants will only bind limited amount of metal ions per circulation through the digester. Post reactive actions will therefore take time to work and make it possible for ions to form compounds and induce scaling on the surfaces, resulting unwanted outcome.

It was also discovered that there are existing coating technologies that can be applied for screen surface. Coating material has several applications that needs to be further studied to find out the most cost-effective and best applicable technology to perform coating. Some of the best potential lay on spraying applications as well as existing coating material films. It is also possible to provide harder surface for the screen by applying primary coating on the screen below to coating material surface with silicon or wolfram-based mixes. These can provide both mechanical as well as chemical durability, in addition to lowering the surface roughness and giving proper surface for coating material to bind on.

7 SUMMARY

This thesis focused on dissolving pulp production and the potential of coating the digester and pre-hydrolysis vessel screens with material which would decrease the scaling issues faced mostly in pre-hydrolysis kraft cooking, especially focusing on the continuous digester process, however the results should be expandable to batch cooking with minor specifications. The first part of thesis was focused to give an overview of current popularity and dominating technologies in dissolving pulp production. Comparison to traditional paper-grade pulp production was also performed.

It was noted that pre-hydrolysis kraft cooking is currently increasingly dominant process over traditional acid sulphite cooking. Both processes were still discussed, as they are two most common dissolving pulp production processes with high importance in the field. End uses of dissolving pulp vary in increasing rate, but still most common end-use is viscose pulp, which is primarily used for textile industry. The rapid conversion with lowering demand in paper and increasing demand for different dissolving pulp end-products has also led to an increasing trend of refining other side-products within same mill site to provide raw material to several industries and development of biorefinery concept on pulp mills. Cotton linters are also used for dissolving pulp production, but it is primarily the raw material of the purest end-uses. The thesis focused on wood-based dissolving pulp production.

The process of pre-hydrolysis kraft process was focused on, and process flow from wood chips to exit from digester was described. Issues that scaling causes within the pulp mill was also reviewed as it gives the basis for the study. Methods to avoid and remove scaling within process surfaces was gone through and it was noted that scaling can be avoided prior it happens and removed after the scaling has occurred. Both chemical and mechanical methods can be applied including process control, mechanical washing and chelant use. In mechanical sense, deactivation of calcium can be used to limit scaling phenomenon on the process. It is also recommended to apply several methods simultaneously in case scaling is occurring in the process.

Process conditions within digester and pre-hydrolysis vessel made limitations for applicable coating materials. Most limiting parameter is pH value, which varies from acidic pre-

hydrolysis to base alkaline cooking within the digester. Temperature variation within the digester vessel is kept as small as possible but well over 100 °C within the cooking and pre-hydrolysis. Other limiting factors can be manufacturing limitations due to properties of coating material, coating possibilities within mill site and hard organic and metal compounds ending up within digester which can cause mechanical damage to screen surface coating.

Fitting methods for performing coating were found from existing applications, primarily spray coating or film applications would seem initially as most valid solution. Primary coating below the surface coating can improve the durability of coating lifetime as well as screen performance.

The study planned for the thesis was not managed to perform due to schedules at mill site, and therefore the evaluation of the screen coating was performed as literature work. Benchmarking should be made between existing, non-coated screens and newly coated screens, comparing scaling and its removability within same process and as similar process conditions as possible. Chemicals used should be from mill that has occurring issues with supersaturation of CaCO_3 in the process, so that test run will have best possible conditions and real-life scenario as reference. It can be, however, as issue to solute CaCO_3 to existing base solution and dissolving acid in liquor can cause unwanted reactions and hazard to test run. Some ideas how to create supersaturated solution were presented in the thesis, with possibility to use water-based solution instead of liquor.

All in all, it should be remembered that coating of the screens can add extra costs to maintenance department but result in major saving in case scaling has caused unplanned shutdowns at mill. When coating can save even one unplanned shutdown of the digester plant, the initial investment for the mill used to screen coating will be paid back multiple times. This however should be initially confirmed with mill-scale test runs to benchmark the screen coating in mills that suffer from scaling, together with general cooking study to assure the nature of the issues and potentially repair other, surrounding process issues that may also have an impact on the digester availability.

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