Dissertation

VTT PUBLICATIONS 767

Anja Leponiemi

# Fibres and energy from wheat straw by simple practice

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Anja Leponiemi. Fibres and energy from wheat straw by simple practice [Kuituja ja energiaa vehnän oljesta yksinkertaisella menetelmällä]. Espoo 2011. VTT Publications 767. 59 p. + app. 74 p.

**Keywords** Non-wood fibre, wheat straw, biorefinery, hot water treatment, mechanical refining, alkaline peroxide bleaching, chemical pre-treatment, storage, assessment, pulp, energy

# Abstract

The overall purpose of this work is to evaluate the possibilities of wheat straw for fibre and energy production and address the question of whether or not it is possible to develop a cost-effective process for producing good quality pulp from wheat straw for current paper or paperboard products. In addition, in light of the green energy boom, the question of whether fibre production could give added value to energy production using wheat straw is addressed.

Due to the logistics of the bulky raw material, the process should be applied on a small scale that determines the requirements for the process. The process should be simple, have low chemical consumption and be environmentally safe. The processes selected for the study were based on an initial hot water treatment. Actual defibration in the "chemical" approach was then performed using a subsequent alkaline peroxide bleaching process or in the "mechanical" approach through mechanical refining. In both approaches, energy can be produced from lower quality material such as dissolved solids or fines.

In this work, one of the primary aims besides the development of the abovementioned process is to investigate the chemical storage of wheat straw which decays easily between harvesting periods and examine its effects on pulping and pulp properties. In addition, the aim of this work is to determine the market potential for non-wood pulp and evaluate non-wood pulp production.

The results showed that the "chemical" approach produced fibres for printing and writing. The quality of the pulp was relatively good, but the chemical consumption at the target brightness of 75% was high, indicating that a chemical recovery would be needed unless the brightness target could be significantly reduced. The "mechanical" approach produced unbleached fibres for fluting and the energy production from fines and dissolved solids generated additional income. The results also showed that it is possible to store wheat straw chemically with formic acid-based chemicals over a year without significant

changes in the chemical composition. The chemical storage can be integrated with the suggested chemical or mechanical defibration process, soda pulping process or any other process utilising non-wood fibres. In China, a clear demand for non-wood-based fibres exists due to a shortage of fibre and also because of the increasing demand for bioenergy. In Europe, the competitiveness of non-wood fibre utilisation will only be established if combined with energy production.

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**Avainsanat** Non-wood fibre, wheat straw, biorefinery, hot water treatment, mechanical refining, alkaline peroxide bleaching, chemical pre-treatment, storage, assessment, pulp, energy

# Tiivistelmä

Tämän työn tavoitteena oli arvioida vehnän oljen käyttömahdollisuuksia kuidun ja energiantuotannon raaka-aineena sekä selvittää, onko mahdollista kehittää kustannustehokas prosessi, joka tuottaisi hyvälaatuista massaa nykyisiin paperi- tai kartonkituotteisiin ja voiko kuiduntuotanto antaa lisäarvoa vehnän oljesta valmistetun vihreän energian tuotantoon.

Vehnän oljen logistiikan vuoksi prosessin tulisi soveltua pieneen mittakaavaan, mikä aiheuttaa vaatimuksia prosessille. Prosessin tulisi olla yksinkertainen ja ympäristöystävällinen ja kemikaalikulutuksen matala. Tutkimukseen valittiin kuumavesikäsittelyyn perustuvat prosessivaihtoehdot, joissa varsinainen kuidutus tapahtuu tämän vaiheen jälkeen joko ”kemiallisesti” alkalisella peroksidivalkaisulla tai ”mekaanisesti” mekaanisella kuidutuksella. Molemmissa prosessivaihtoehdoissa energiaa voidaan tuottaa kuiduksi kelpaamattomasta materiaalista, kuten liuenneesta kuiva-aineesta tai hienoaineksesta.

Tämän työn tavoitteena oli prosessikehityksen lisäksi tutkia korjuukausien välillä helposti pilaantuvan vehnän oljen kemiallisen varastoinnin vaikutuksia massan valmistukseen ja ominaisuuksiin. Lisäksi tavoitteena oli selvittää non-wood-massan markkinapotentiaalia ja arvioida valmistetun massan tuotantoa.

Tulokset osoittivat että ”kemiallisella” prosessivaihtoehdolla voidaan tuottaa kuituja kirjoitus- ja painopapereihin. Valmistetun massan laatu oli suhteellisen hyvä mutta kemikaalikulutus 75 % tavoitevaaleuteen nähden korkea, mikä tarkoittaa, että kemikaalien talteenottoprosessi tarvitaan, ellei kemikaalikulutusta voida alentaa merkittävästi. ”Mekaanisella” prosessivaihtoehdolla voidaan valmistaa valkaisemattomia kuituja flutingin valmistukseen ja samalla saada energian valmistuksella hienoaineesta ja liuenneesta kuiva-aineesta lisätuloa.

Tulokset osoittivat myös, että vehnän olkea voidaan säilöä kemiallisesti muurahaishappopohjaisilla kemikaaleilla yli vuoden ilman merkittäviä muutoksia kemiallisessa koostumuksessa. Kemiallinen varastointi voidaan integroida

esitettyyn kemialliseen tai mekaaniseen kuidutusprosessiin, soodakeittoprosessiin tai mihin tahansa prosessiin, joka hyödyntää yksivuotisia kasveja. Kroonisen kuitupulan ja lisääntyvän bioenergian tarpeen vuoksi Kiinassa on selvä tarve non-wood-kuiduille. Euroopassa non-wood-kuitujen hyödyntäminen on mahdollista vain, jos se voidaan yhdistää energian tuotantoon.

# Academic dissertation

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# Preface

This thesis was carried out between 2006 and 2010 at the Department of Forest Products Technology in the Aalto University School of Chemical Technology, Finland. I am grateful to Research Professor Allan Johansson and Research Professor Kai Sipilä for their interest and invaluable advice throughout the making of this work. I also want to thank Professor Olli Dahl for the opportunity to write this work. Professor Adriaan van Heiningen and Professor Herbert Sixta are also thanked for their invaluable comments and interest.

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# List of publications

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III Mustajoki, S., Leponiemi, A. and Dahl, O. (2010). Alkaline peroxide bleaching of hot water treated wheat straw. Bioresources 5(2), pp. 808–826.

IV Leponiemi, A., Pahkala, K. and Heikkilä, T. (2010). Storage of chemically pretreated wheat straw – A means to ensure quality raw material for pulp preparation. Bioresources 5(3), pp. 1908–1922.

V Leponiemi, A., Johansson A. and Sipilä, K. (2011). Assessment of combined straw pulp and energy production. Bioresources 6(2), pp. 1094–1104.

# Author's contribution

The author contributed to each of the publications in the following ways:

I Anja Leponiemi wrote the manuscript based on the literature study.

II, IV Anja Leponiemi was responsible for the experimental design, performed or supervised the experimental work, analysed the results and wrote the manuscript.

III Anja Leponiemi was mainly responsible for the experimental design, supervised the experimental work, analysed the results and wrote the manuscript as an equal author with Suvi Mustajoki.

V Anja Leponiemi was responsible for the experimental design, performed or supervised the experimental work, analysed the results and wrote most of the manuscript.

# Contents

# List of abbreviations

| | |
|---|---|
| 06Straw | Wheat straw grown during the summer 2006 |
| 07Straw | Wheat straw grown during the summer 2007 |
| 08Straw | Wheat straw grown during the summer 2008 |
| ADt | Air dry ton |
| ALCELL | Alcohol cellulose, a pulping process using ethanol as the sole pulping chemical |
| AQ | Anthraquinone |
| ASAE | Alkaline sulphite-anthraquinone-ethanol pulping process |
| ASAM | Alkaline sulphite-anthraquinone-methanol pulping process |
| BDt | Bone dry ton |
| BHKP | Bleached hardwood kraft pulp |
| BIVIS | Chemi-mechanical or semichemical twin screw extrusion pulping process |
| CIMV | Compagnie Industrielle de la Matière Végétale (Industrial Company for Vegetal Material), an organosolv pulping process using acetic acid and formic acid as the cooking chemicals |
| DTPA | Diethylenetriaminepentaacetic acid |
| EPC | Engineering, procurement and construction |
| EU | European Union |
| FAO | Food and Agriculture Organisation of the United Nations |

| | |
|---|---|
| FBB | Folding boxboards |
| FreeFiber | Alkaline pulping process using sodium carbonate impregnation prior to cooking in gaseous methanol |
| HPAEC | High-performance anion-exchange chromatography |
| HWT | Hot water treatment |
| IDE | Impregnation-depolymerisation-extraction, an alkaline pulping process using sodium carbonate, ethanol and anthraquinone as the cooking chemicals |
| ISO | International Organisation for Standardisation |
| NACO | Alkaline pulping process using sodium carbonate, oxygen and sodium hydroxide as the cooking chemicals in a digester called Turbo pulper |
| NaOH | Sodium hydroxide |
| $Na_2CO_3$ | Sodium carbonate |
| NSSC | Neutral sulphite semichemical process |
| OCC | Old corrugated containers |
| P | Alkaline peroxide bleaching stage |
| $P_1$ | First alkaline peroxide stage |
| Paa | Peracetic acid bleaching stage |
| Punec | Pulping method using ethanol, anthraquinone and caustic soda as the cooking chemicals |
| SAICA | Spanish paper company Sociedad Anónima Industrias Celulosa Aragonesa, an alkaline semichemical pulping process using sodium hydroxide as the cooking chemical |
| SCAN | Scandinavian Pulp, Paper and Board Testing Committee. |
| WLC | White-lined chipboards |

# 1. Introduction

## 1.1 Non-wood pulp production

Non-wood fibres have a long history as a raw material for papermaking. Paper was first made in 105 AD in China (Clark 1985b, Atchison & McGovern 1987). It was produced from textile wastes, old rags, used fish nets, mulberry bark and grass (Clark 1985b, Atchison & McGovern 1987).

Non-woods were used as a raw material for paper for the following 1700 years. In the second half of the 19th century the supply of annual plant fibre raw materials and textile rags was no longer sufficient to satisfy the fibre raw material demand in Europe and the USA. This shortage prompted the development of several methods of making paper fibres from wood. In 1860, the first pulp mill using the soda process was established in the USA. Several mills were also built in Europe in the 1860s and 1870s. Wood was quickly established as the primary source of fibre for papermaking. (Gullichsen 2000).

Today, non-wood pulp accounts for approximately 10% of the global pulp production for papermaking; see Table 1 (FAOSTAT Forestry 2010). China produces more than two-thirds of the non-wood pulp produced worldwide, while non-wood production is relatively insignificant in Europe, America and Africa (FAOSTAT Forestry 2010). The most widely used non-woods for papermaking are straw, reed, bamboo and bagasse (Atchison 1996, Pöyry 2006). According to FAO statistics (FAOSTAT Forestry 2010), in 2009 the total worldwide production of the “other fibre pulp” was 19.1 million tonnes, while total pulp production for paper totalled 178.1 million tonnes. “Other fibre pulp” is mainly non-wood pulp, but some data collection systems may report recycled pulp as “other fibre pulp”. This seems to be the case when reviewing European figures since only one operating non-wood mill in Europe is reported. The Dunacell mill, located in Dunaújváros, Hungary, produces 23,000 t/a bleached flax and straw sulphate (Pöyry 2010).

Table 1. Pulp production in year 2009. Pulp for paper includes chemical, mechanical and semichemical wood pulp as well as “other fibre pulp” which is mainly non-wood pulp. (FAOSTAT Forestry 2010).

| | “Other fibre pulp” Million tonnes | Pulp for paper Million tonnes |
|---|---:|---:|
| European Union | 1.4 | 37.0 |
| Europe | 1.4 | 45.6 |
| North America | 0.3 | 64.2 |
| South America | 0.5 | 20.9 |
| Asia | 16.7 | 42.2 |
| - China | 13.4 | 20.5 |
| - India | 2.0 | 4.0 |
| Africa | 0.2 | 2.2 |
| Oceania | 0.0 | 2.7 |
| World | 19.1 | 178.1 |

As can be seen in Figure 1, papermaking fibre consumption is forecast to grow by 1.9% in the long term. This means that the 390 million tonnes consumed in 2009, including recovered paper, will increase to approximately 480 million tonnes in 2020. In addition, non-wood based pulp produced using sustainable and environmentally friendly methods will retain its position as an important fibre source in Asia (Kuusisto 2010).

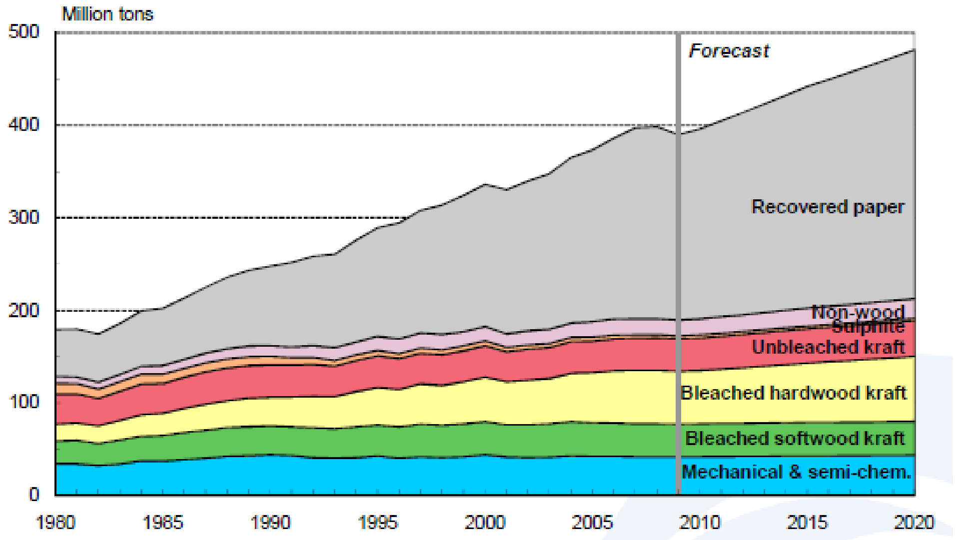

Figure 1. World consumption of papermaking fibres, 1980–2020 (Kuusisto 2010).

## 1.2 Non-wood resources

One of the characteristics of non-wood fibres is the much wider range of fibre lengths in different species (Atchison 1987). Many of these fibres, such as straws, reeds and bagasse, are similar in length to the short fibre hardwoods. On the other hand, others such as flax and hemp are so long that they have to be shortened prior to papermaking (Atchison 1987). From a quality point of view, any grade of paper can be produced by the combination of different non-wood plant fibres (Atchison & McGovern 1987). For instance, flax has a very long fibre length and thus good reinforcement properties. Less than 10% of flax pulp in the mixture would give sufficient reinforcement for short fibre pulp as shown in earlier studies (Leminen et al. 1996). Therefore, through careful selection of the raw material, the desired paper properties can be achieved from a very wide range of fibre lengths.

Non-wood raw materials can be obtained as a by-product of food production or from naturally growing plants, a major part of which are cultivated just for fibre production, see Figure 2. Typically, the entire plant is used for fibre production with grass fibres such as reed or straw. The bast fibres such as hemp and flax are separated from the stem by retting or decortication. Leaf fibres are obtained from the very long leaves of some monocotyledons such as abaca and sisal. The most important fruit fibre is cotton, the fibre of which is obtained from the seed hair of the plant by ginning (Ilvessalo-Pfäffli 1995).

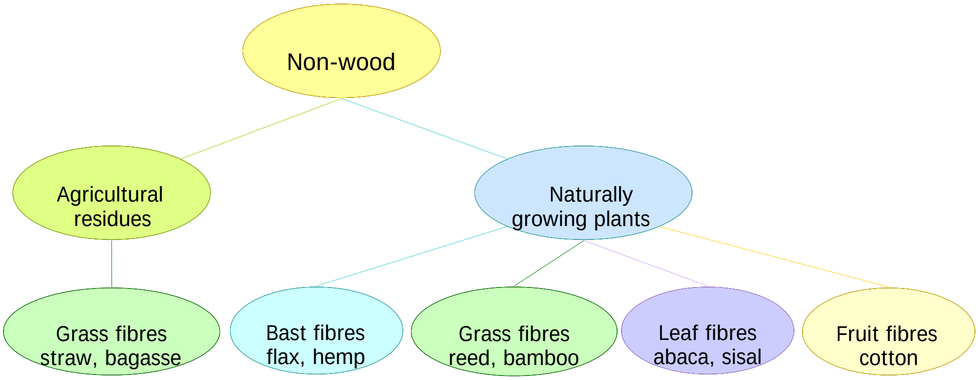

Figure 2. The classification of non-wood fibres (adapted from Ilvessalo-Pfäffli 1995).

As shown in Table 2, the area of agricultural land worldwide is larger than that of forests (FAOSTAT Resources 2009). Furthermore, non-wood fibres usually have high annual biomass yields per hectare which are equal or superior to that of woods (Pierce 1991). Approximately 30% of the forest area is used primarily for the production of wood. An additional 24% of the forest area is designated for multiple uses, which also includes the production of wood in most cases (FAO 2010).

Table 2. Agricultural area versus forest area in year 2007 (FAOSTAT Resources 2009).

| | Agricultural area Million hectares | Forest area Million hectares |
|---|---|---|
| European Union | 190 | 157 |
| Europe | 474 | 1003 |
| North America | 479 | 614 |
| South America | 580 | 823 |
| Asia | 1663 | 574 |
| - China | 553 | 205 |
| - India | 180 | 68 |
| Africa | 1157 | 627 |
| Oceania | 440 | 206 |
| World | 4932 | 3937 |

## 1.3 Non-wood pulping processes

Various alkaline, semichemical, organosolv and other methods have been developed for non-wood pulping but many of them are tested only in laboratory environments. Paper I reviews in more detail the recent developments in the chemical and chemi-mechanical non-wood pulping processes and the advantages and disadvantages of these systems. No remarkable breakthrough has occurred in recent decades in the field of non-wood pulping, excluding the Chempolis and CIMV process development.

Traditionally non-wood pulps were produced by alkaline processes. Alkaline processes such as soda (Mohta et al. 1998, Tutus & Eroglu 2003, Feng & Alen 2001, Finell & Nilsson 2004, Okayama & Li 1996) and the NACO process (Recchia et al. 1996, Fiala & Nardi 1985, Paul 2001) have been used to produce non-wood pulp in mills. The main problem with alkaline processes for non-wood fibres is that silicates of non-wood plants dissolve during cooking into the cooking liquor. The presence of silicate ions causes serious problems in recovery such as scaling on the heat transfer surfaces in the evaporator, high viscosity of the concentrated liquor and also problems in causticising (Myreen 2001). High viscosity of concentrated liquor has a negative influence on both evaporation and combustion (Myreen 2001). On a small scale, the chemical recovery or effluent treatment is really a technical and economical challenge (Rangan & Rangamannar 1997). Due to this, many small non-wood pulp mills have no chemical recovery system, which has presented an excessive burden on local environments and has led to the closure of mills.

The semichemical process SAICA (Lora & Escudero 2000) and chemi-mechanical Bivis process (Westenbroek & van Roekel 1996, Roberts 2000, Westenbroek 2004) have also been used for mill-scale non-wood pulp production. The chemical consumption of these processes is lower than in chemical processes, nevertheless the spent liquor must be incinerated or treated biologically. Some mills in China have used the neutral sulphite semichemical (NSSC) process (Nassar 2004, Savcor Indufor 2006, Pöyry 2006) for containerboard production. Environmental issues are a problem with this process as well.

Various organosolv methods have been developed but many of them have not progressed past the laboratory test stages. Methods based on organic acids or alcohols have been tested at pilot level more often. An advantage of organosolv processes is the formation of useful by-products such as furfural, lignin and hemicelluloses. These processes would most probably benefit from larger mill sizes.

The first small-scale agro-fibre mill based on a CIMV organosolv process is scheduled to begin operations from the end of 2010 in Loisy sur Marne near Vitry le Francois, France. CIMV Marne will treat 180,000 tonnes of wheat and barley straw per year and produce bleached chemical pulp for printing and writing, low molecular weight lignins and C5 sugar syrup (Delmas 2010). In addition, Chempolis (Chempolis 2010) recently announced that a licence and EPC agreement (Engineering, Procurement and Construction) has been signed with Tianjin Jiuqian Paper Co Ltd to supply three biorefineries, each with a capacity of 100,000 t/a of bleached wheat straw pulp. The new Chempolis plants are scheduled to begin operations in 2012–2013 (Chempolis 2010).

The CIMV process uses acetic acid and formic acid as the cooking chemical (Lam et al. 1999, Delmas et al. 2003, Lam et al. 2004, Kham et al. 2005a, Kham et al. 2005b, Lam et al. 2005, Mire et al. 2005, Benjelloun Mlayah et al. 2006, Delmas et al. 2009). The acids dissolve lignins and hydrolyse the hemicelluloses into oligo- and monosaccharides with high xylose content. The raw pulp is then filtered, the solvent is removed and the pulp is bleached with hydrogen peroxide (Delmas 2008). Organic acids are recycled from waste liquor via evaporation.

Water is used to treat the remaining syrup to precipitate lignins, which are then separated (Delmas et al. 2006).

The Chempolis process is also based on using formic and acetic acid (Rousu & Rousu 2000, Rousu et al. 2003, Anttila et al. 2006) as cooking chemicals to produce pulp, biochemicals and biofuels from non-wood raw materials. Formic acid is the main component in cooking liquor. After cooking, the pulp is washed and pressed in several stages with formic acid. The last washing stage is performed at a high pulp consistency with performic acid. Then, the pulp is bleached with alkaline peroxide. Spent cooking liquor can be evaporated to 90% dry solids and incinerated. The evaporation is accompanied by the formation of formic acid, acetic acid and furfural. Forming formic acid is claimed to reduce the demand for make-up formic acid. Formic acid, acetic acid and furfural are volatile compounds which can be separated from evaporation condensates by distillation (Anttila et al. 2006). However, organic acids, especially formic acid, are highly corrosive and may cause severe corrosion problems in process equipment.

High cooking temperature and thus high pressure is needed when alcohols are used as cooking chemicals. Methanol has been used as an additive in kraft, sulphite and soda pulping. However, the use of methanol may be hazardous, since methanol is a highly flammable and toxic chemical. Demonstration plants using the alkaline sulphite-anthraquinone-methanol process (ASAM) (Patt & Kordsachia 1986, Khristova et al. 2002, Patt et al. 1999) and the soda pulping method with methanol (Organocell) (Schroeter & Dahlmann 1991) have been built. The active cooking chemicals of the ASAM process are sodium hydroxide, sodium carbonate and sodium sulphite. The addition of methanol to the alkaline sulphite cooking liquor improves delignification considerably and the process produces pulp with better strength properties, higher yield and better bleachability compared with the kraft process (Patt & Kordsachia 1986, Khristova et al. 2002).

A new process, the FreeFiber process, is being developed by Metso (Enqvist et al. 2006, Boman et al. 2010). This process involves sodium carbonate impregnation prior to vapour phase cooking in gaseous methanol. The process does not present obvious economic advantages at the moment but the pulp properties are claimed to be attractive enough for further investigation (Savcor Indufor 2007).

The health risks of ethanol are lower and thus several processes based on ethanol have been developed. The alkaline sulphite-anthraquinone-ethanol

(ASAE) process (Usta et al. 1999), the IDE process (Westin et al. 2000, Hultholm et al. 1995, Hultholm et al. 1997) and Punec process (Khanolkar 1998) use ethanol as an additive in alkaline cooking. The ALCELL (alcohol cellulose) process (Pye & Lora 1991, Winner et al. 1997) uses an aqueous solution of ethanol as the sole delignifying agent.

Despite a variety of processes and the availability of raw-material sources, the widespread utilisation of annual plants in pulping has not been technically or economically feasible in Western countries due to the lack of a simple and environmentally efficient pulping method and the problems associated with raw material storage and logistics.

An ideal non-wood pulping process is simple and environmentally efficient and can be applied on a small scale. Essential to the process is whole chain utilisation of agro-fibres; where the most valuable proportion would be used for human or animal food or commodity production, the second most valuable proportion of the plant would be utilised as a raw material in traditional papermaking and the least valuable proportion and non-recyclable waste paper would then be utilised directly for energy production. (Paper I).

A non-wood pulping process involving hot water treatment under mildly acidic conditions has been proposed (Lindholm et al. 1995, Leminen et al. 1996, Johansson et al. 2000, Edelmann et al. 2000) for non-wood pulp production. The idea of the process is to utilise the low lignin content and the unique loose structure of the annual plants. First, the raw material is treated with mildly acidic liquor containing a mixture of formic and acetic acids, and chelating agents in a low temperature, un-pressurised stage (Johansson et al. 2000). The actual defibration then takes place in subsequent alkaline peroxide bleaching (Johansson et al. 2000). This simple process can be applied on a small scale without a recovery. The effluents from the mild acid cooking and bleaching stages can be treated in traditional biological effluent treatment systems, for instance. In the case of wheat straw, a pulp with an ISO brightness of over 80% and a yield of over 50% is achieved (Johansson et al. 2000). Silica is partly extracted into the bleaching effluents. The method offers an interesting way for economically competitive small-scale pulping processes for non-wood materials.

## 1.4 Challenges in non-wood processing

The main problems associated with using industrially non-wood materials are the logistics of the bulky raw material and its typically short harvesting time

(Clark 1985a). Thus, the raw material must be stored between harvest seasons. If the raw material is stored outside under prevailing climate conditions, moisture and biological activity easily cause the material to decay. In addition, non-wood plants usually have a high silica content and the silicates dissolve in alkaline cooking liquor which makes alkaline recovery difficult (Myreen 2001) and in many cases places an excessive burden on the local environment. Finally, the poor drainage of produced non-wood pulp results in low production rates (Cheng et al. 1994).

Typically the processes are adapted from wood processing which benefit from the larger mill size (Paper I). However, concerns associated with the local availability of non-wood raw material force pulp mills to remain small and thus lead to the need for processes to be as simple as possible in order to be competitive unless very valuable by-products can also be extracted.

The benefits of utilising agro-fibres are their generally lower lignin content compared with woods (Grant 1958, Hurter 1988). Generally, non-woods are easier to pulp and thus are cooked at low temperatures with lower chemical charge. From a farming and agro industrial point of view, non-food applications can generate additional income alongside income from food crops or cattle production. In addition, paper production from non-wood fibres could help in reducing the need to procure pulpwood from natural forests and the requirement for large-scale plantations (Pande 1998). To conclude, annual plants are a potential raw-material source for the chemical pulping industry.

# 2. Objectives and outline of the study

The hypotheses of this work are that in future there will be a clear demand for non-wood-based fibres at least in China and that the combined production of fibres and energy is more cost effective than the production of energy alone. In actual fact, no satisfactory process exists which could solve all of the traditional problems related to non-wood pulping. Therefore, this work concentrates on eliminating the main problems related to non-wood pulping such as the silica problem, the availability of high-quality raw materials throughout the year and low drainability due to the high fines content.

The main objective of this work is to develop an economically viable process for producing papermaking fibres of adequate quality and generating energy from wheat straw. Wheat straw was selected as the raw material since wheat is cultivated and available worldwide (Curtis 2002) and only a minor part of the straw is used for energy production or animal feed. One of the primary aims in this work is to find ways to store the raw material chemically between the harvesting periods and examine the effects on pulping and pulp properties (Paper IV). In addition, the aim of this work is to determine the market potential for non-wood pulp and evaluate its production (Paper V). The study also included the literature review (Paper I).

Two approaches were selected for the study, both of which were based on an initial hot water treatment: the “chemical” where bleached pulp is produced for printing and writing papers by hot water treatment and the following alkaline peroxide bleaching (Paper II–IV) and the “mechanical” where the unbleached material from the hot water treatment stage is mechanically refined (Paper II, V) to produce fibres for packaging grade papers. In the future, the straw fibre could be considered as a raw material for biocomposites. In both approaches, the idea is that the lower quality material produced, such as dissolved solids or fines, is used for energy production.

# 3. Experimental

An overview of the research plan is shown in Figure 3. Paper I covers the background in the form of literature review. Paper II focuses on the optimisation of hot water treatment prior to alkaline peroxide bleaching and on the mechanical refining of hot water treated straw. Paper III focuses on the optimisation of alkaline peroxide bleaching and Paper IV focuses on the chemical pre-treatment/storage of wheat straw. Paper V evaluates the obtained results. The materials and methods used in the experiments are described in detail in the Papers; this chapter gives a more general overview of the experimental design.

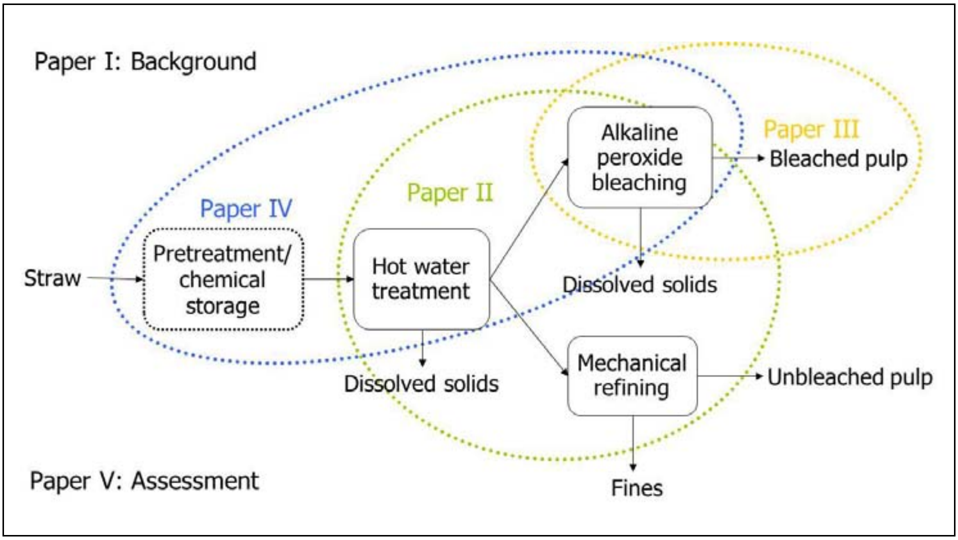

Figure 3. Overview of research plan.

## 3.1 Raw material

The spring wheat straws used in the experiments were cultivated in Jokioinen, Finland, in summer 2006 (06Straw), 2007 (07Straw) and 2008 (08Straw). The wheat varieties were Kruunu in 2006, Marble in 2007 and Kruunu in 2008. The wheat was grown on a sandy clay field in Jokioinen, Finland (60°49'12"N, 23°28'12"E). The 06straw was used in the hot water treatment temperature optimisation and the 07straw in the mechanical refining experiments. 06Straw and 07Straw were used in the optimisation of alkaline peroxide bleaching. In addition, the 07Straw and the 08Straw were used in the chemical pre-treatment/storing experiments.

The 06Straw (Paper II, III) and the 07straw (Paper III, IV) were harvested and cut to 5 cm and dried to 90% dry content. The fines were removed by screening according to standard SCAN-CM 40:88. The screening time was 30 s and pieces over 6 mm were accepted for the experiments. The 08Straw (Paper IV) was baled with a chopper baler and treated with formic acid based solution AIV 2 Plus preservative from Kemira Oyj (76% formic acid, 5.5% ammoniumformate, water) one day after threshing; the targeted amount was 9 mL/kg of fresh straw. The distance between baler’s knives were 8.6 cm, and the resulting straw length was 4–10 cm. Additionally, some 07Straw and 08Straw were collected after threshing and cut into pieces with a laboratory cutter for the chemical storing experiments.

## 3.2 Hot water treatment and alkaline peroxide bleaching

The hot water treatment optimisation was carried out over the temperature range 70–150°C (Paper II). For temperatures above 100°C the treatment was carried out in an air-heated digester equipped with six 2.5 L autoclaves. Treatments below 100°C were carried out in polyethylene bags in a water bath. The time at treatment temperature was 60 min with the exception of a 150 min treatment time which was also tested for selected test points. The water to straw ratio was 10. The acid charge in hot water treatment was 0–2.3% on the straw. The acid was a mixture of formic (25%) and acetic acid (75%). Diethylene-triaminepentaacetic acid (DTPA, charge 0.2% on straw) was used as a chelating agent in the treatments. After the treatment, the straw was washed with deionised water and then bleached with P-P-Paa-P sequence in polyethylene bags in a water bath. P is an alkaline peroxide and Paa a peracetic acid stage.

The objective of alkaline peroxide bleaching optimisation (Paper III) was to achieve a brightness of 75% ISO, with minimal sodium hydroxide consumption, whilst retaining the pulp properties. The variables studied were the pressurisation of the first peroxide ($P_1$) stage with oxygen, the substitution of sodium hydroxide partially with sodium carbonate and a mild alkali treatment before the actual peroxide bleaching. In addition, the role of sugars in the bleaching stages was studied by adding glucose or xylose to the $P_1$ stage. The bleaching conditions are presented in Paper III.

The bleaching conditions for the reference pulps and for all the other experiments, including reaction time, reaction temperature, and chemical dosage, are presented in Table 3. When calculating the bleaching chemical dosages for the following bleaching stage, it was assumed that there were no yield losses. Only the amount of the pulp used for defining dry matter content and ISO brightness were deducted from the original amount of pulp. However, the yield losses were taken into account when calculating the bleaching consistency.

Table 3. Bleaching conditions of reference, pressurised $P_1$, sugar addition and alkali pretreatment pulps. Consistency 10%, temperature in $P_2$, Paa and $P_3$ stages 85˚C, and time in $P_2$ and $P_3$ stages 180 min and in peracetic acid stage 60 min. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. $PP_1$ = pressurised $P_1$ stage, APT = NaOH pretreatment and PPT = $O_2$ pressurised NaOH pretreatment.

| | | Ref. bleaching | Pressurised $P_1$ | Sugar addition | Alkaline pretreatment | $O_2$ pressurised alkaline pretreatment |
|---|---|---|---|---|---|---|
| | | Low / high chem | $PP_1$ 95°C 120 min / $PP_1$ 105°C 60 min / $PP_1$ 105°C 120 min | Low / medium / high chem | APT 2% NaOH / 2.5% NaOH seq. P-P-Paa-P / P-Paa-P | PPT 3% NaOH 60 min / 3% NaOH 90 min / 4% NaOH 90 min |
| Alkaline pretreat-ment | Pressure (bar) | - | - | - | - | 3 |
| | Temp. (°C) | - | - | - | 85 | 95 |
| | Time (min) | - | - | - | 180 / 240 | 60 / 90 / 90 |
| | NaOH (%) | - | - | | 2.0 / 2.5 | 3.0 / 3.0 / 4.0 |
| $P_1$ | NaOH (%) | 7.0 / 8.5 | 6.0 / 6.0 /6.0 | 7.0 / 8.0 / 8.5 | 3.5 / 2.5 | 3.0 |
| | $H_2O_2$ (%) | 4.0 / 5.0 | 4.0 / 4.0 / 4.0 | 4.0 / 5.0 / 5.0 | 3.0 | 2.0 |
| | Temp. (°C) | 85 | 95 / 105 / 105 | 85 | 85 | 85 |
| | $O_2$ pressure (bar) | - | 3 | - | - | - |
| | Time (min) | 60 | 120 / 60 / 120 | 60 | 60 | 60 |
| | $MgSO_4$ (%) | - | 0.3 / 0.3 / 0.3 | - | - | - |
| | DTPA (%) | - | 0.2 / 0.2 / 0.2 | - | - | - |
| | Sugar (mg/L) | - | - | 150 | - | - |
| $P_2$ | NaOH (%) | 1.0 / 1.5 | 1.5 / 1.0 / 1.0 | 1.0 / 1.0 / 1.5 | 0.75 / - | 0.5 |
| | $H_2O_2$ (%) | 2.0 | 2.0 / 2.0 / 2.0 | 2.0 | 2.0 / - | 2.0 |
| Paa | NaOH (%) | 0.2 | 0.2 / 0.5 / 0.5 | 0.2 | 0.2 | 0.2 |
| | Peracetic acid (%) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| $P_3$ | NaOH (%) | 1.0 / 1.5 | 1.0 | 1.0 / 1.5 / 1.5 | 0.75 | 0.75 |
| | $H_2O_2$ (%) | 2.0 | 2.0 | | 2.0 | 2.0 |
| Acidifi-cation | $SO_2$ (%) | 0.8 / 1.1 | 1.1 / 0.7 / 0.9 | 0.4 / 0.7 / 0.7 | 0.5 | 0.5 / 0.4 / 0.4 |

## 3.3 Hot water treatment and mechanical refining

The straw for mechanical refining experiments (Paper II) was treated in a rotating 16 L digester. The hot water treatment temperature was 120°C and time at treatment temperature 60 min. No chemicals were added. After the hot water treatment, the straw was washed and then refined with the batch type VTT wing refiner at 120°C and 1500 r/min. The coarse fraction was separated with a Valmet TAP03 laboratory screen with the slot size of 0.13 mm. The coarse fraction was refined again.

The mechanically refined pulp after hot water treatment was fractionated with a Bauer McNett apparatus. 100 and 200 mesh fractions were combined for paper technical properties analysis and for alkaline peroxide treatment. The alkaline peroxide treatment was performed in a polyethylene bag in a water bath. The conditions were 85°C, 3 h, consistency 10%, 5% NaOH, 4% $H_2O_2$, 0.25% $MgSO_4$, and 0.2% DTPA.

In addition, some extra test points at a higher 170°C temperature was performed with corresponding methods in the wing refiner of the Aalto University, Department of Forest Products Technology (Paper V). The speed of rotation was 60 r/min. The alkaline peroxide treatment conditions of unfractionated refined straw were 85°C, 180 min, consistency 10%, 2% NaOH, 4% $H_2O_2$.

## 3.4 Soda cooking

Soda cooking (Paper II, IV)) was performed in a 2.5 L autoclave of the air-heated digester. The cooking temperature was 160°C, time at cooking temperature 60 min, NaOH charge 14% and liquor to straw ratio 5:1.

## 3.5 Chemical pre-treatment/storage

Urea (40% solution), formic acid (85% solution) or formic acid-based solution AIV 2 Plus preservative from Kemira Oyj (76% formic acid, 5.5% ammoniumformate, water) was used as a pre-treatment/storage chemical. The use of these chemicals is standard procedure in agriculture. The experiments were performed in Plexiglass® acrylic silo trials, round bales or minisilos (Paper IV).

The formic acid charge was 15 g per kg of dry straw matter, the urea charge was 44 g per kg of dry straw matter and the formic acid based preservative charge was applied at the rate of 9 mL per kg of fresh straw. Straw and chemical were mixed carefully before weighing the mixture into the silos. The acid was applied during baling using a pump applicator attached to the baler. After the baling, the straw was wrapped with white stretch film.

The dry content of the chopped 07Straw was 74.4%. The dry matter content of the fresh 08Straw was 85.4%. The dry content of the straw in minisilos was adjusted with mixture of water and preservative solution to 75%.

Straw and chemical were mixed carefully before weighing the mixture into the silos. The straw amount was 900 g in the Plexiglass® Acrylic Silo experiments or 32 g in the minisilo experiments including the weight of added acid or urea. The round bales weighed approximately 229 kg excluding the wrapping.

The time of storage in Paper IV varied from about two months to one year. In addition to this, one round bale and two minisilos were tested after 1.5 years of storage. After the period of storage, the silos were opened and the straw was washed. The bales were frozen directly after sample collection and were not washed before further use.

## 3.6 Analyses

The bleached pulps were screened prior to sheet preparation. All analyses were performed according to ISO and SCAN standards, except for the carbohydrate analysis of straw which was done by high-performance anion-exchange chromatography (HPAEC). The ashing was conducted at 550°C for 12 h.

The mechanically refined pulp after hot water treatment was fractioned with a Bauer McNett apparatus. The paper technical properties were determined from the combined 100 and 200 mesh fractions. In addition, the properties of the mechanical wheat straw pulp reinforced with softwood pulp were analysed. The softwood pulp was beaten for 10 min with a Valley Hollander and the proportions of wheat straw pulp were 0, 20, 40, 60, 80 and 100%.

# 4. Results

## 4.1 Processes

This study includes the development of two approaches for pulp and energy production from wheat straw, both based on initial hot water treatment. In the “chemical” option the straw is defibrated in the following hot water treatment and in the mechanical the defibration is performed by the mechanical energy. Due to the moderate conditions, only 10% of original wheat straw material dissolves during hot water treatment at 90–120°C temperature (Paper II). If the temperature is increased to 170°C, approximately 30% of the original raw material dissolves (Paper V), see Figure 4. In industrial operations, these dissolved solids could then be utilised for energy production such as biogas.

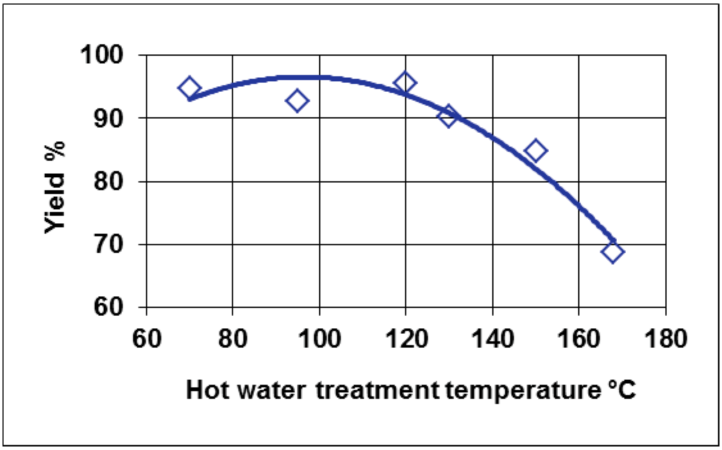

Figure 4. The effect of the hot water treatment temperature on the yield. Wheat straw 2007, time at temperature 60 min. (Paper V).

The chemical composition, especially the lignin content, does not significantly change during treatment at 70–130°C temperature (Paper II). About 1/3 of the yield loss comes from the reduction of ash content. Some water soluble carbohydrates are also dissolved during hot water treatment.

Despite the small changes in chemical content with the hot water treatment, this stage is needed before peroxide bleaching. The defibration of the straw was remarkably worse without the prior hot water treatment and the final brightness was about 5% lower compared with the optimum hot water treated and bleached pulp (Paper II). Furthermore the rejects content of the bleached pulp was 21.6%, approximately three times more than the amount of rejects obtained when the hot water treatment was used (Paper II). In addition to the cleaning effect, the hot water treatment appears to “soften” the wheat straw material before the following bleaching stage (Paper II).

### 4.1.1 Bleached pulp for printing and writing

When the hot water treatment is combined to alkaline peroxide bleaching it is possible to produce a chemical type of pulp for writing and printing papers or for cartonboards such as folding boxboards (FBB) and white-lined chipboards (WLC) (Paper II–V). Fully bleached pulp is not necessarily required for these purposes. Hence, the brightness target in this study was 75% ISO.

Figure 5 presents the brightness of the reference pulps produced from the straws grown during different years. The straws grown during different years have a different chemical composition, and therefore, the amount of chemicals required in bleaching varies (Paper III). The 2006 straw (06Straw) required fewer chemicals to be bleached to 75% ISO brightness than the 2007 straw (07Straw). The quality of pulp is comparable to that of soda pulp (Paper I, III) even though the pulp properties from the different straws varied slightly. The pulp from Straw06 had better optical and strength properties and lower bulk than the reference pulp from Straw07 with the same bleaching conditions (Paper III).

Figure 6 presents the yield of the reference bleachings after each bleaching stage of sequence P-P-Paa-P. The pulps with the lowest chemical dosage had the highest yield, as expected. Generally a yield level above 50% is considered to be advantageous. The yield reduction in the alkaline peroxide bleaching results from the dissolution of carbohydrates and ash, but lignin is also partly dissolved.

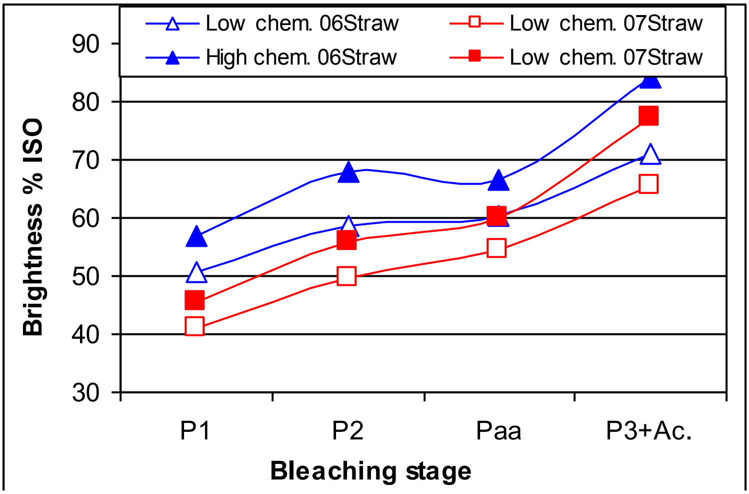

Figure 5. Brightness of reference pulps after each bleaching stage. Raw material 06Sstraw and 07Straw. Hot water treatment of straw at 120°C for 60 min followed by P-P-Paa-P bleaching (Paper III).

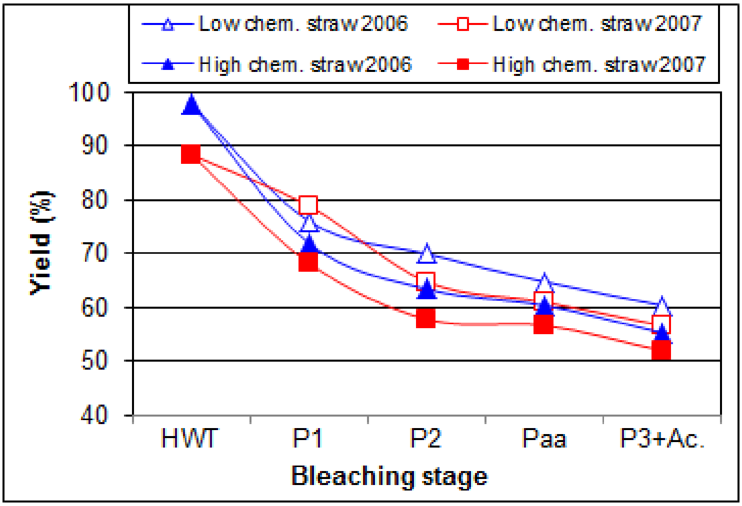

Figure 6. Yield of reference pulps after each bleaching stage; raw material 06Straw and 07Straw. Hot water treatment of straw at 120°C for 60 min followed by P-P-Paa-P bleaching (Paper III).

The process consumed high amounts of sodium hydroxide in bleaching. In practice this means that the process would need some kind of chemical recovery system unless the bleaching chemical consumption could be notably reduced. The possibilities to reduce the sodium hydroxide consumption were studied.

By a mild alkali treatment before the actual peroxide bleaching the total sodium hydroxide consumption can be reduced from a level of 9–11.5% to 6–7% (Paper III), see Figure 7. However, such a reduction clearly decreased the final brightness (15 to 24% ISO) although at the same time a higher yield (1.2–11.1% units) was obtained compared to the reference pulp. The alkali charge was not sufficient to defibrate the straw as well as the reference pulp, and the process may need a moderate mechanical treatment to be combined with the bleaching. The pulp properties were not significantly impaired, even though the yield of these pulps was higher and the bondability and thus the tensile index somewhat lower, see Table 4 (Paper III). If the brightness was not the main issue, then a pulp with acceptable properties could be achieved.

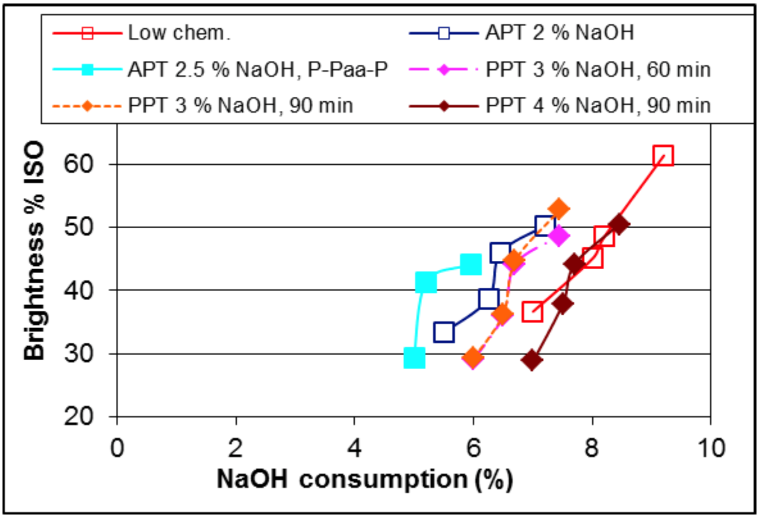

Figure 7. Brightness of alkali pre-treatment bleachings and reference pulp as a function of NaOH consumption. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by APT/PPT-P-P-Paa-P bleaching. Low chem reference pulp with 9% NaOH charge, APT alkali pre-treatment, PPT pressurised alkali pre-treatment (Paper III).

Table 4. Paper Technical Properties of Reference and Alkali Pretreatment Bleaching Paper Sheets. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by APT/PPT-P-P-Paa-P bleaching. Low chem reference pulp with 9% NaOH charge, high chemical reference pulp with 11.5% NaOH charge, APT alkali pretreatment, PPT pressurised alkali pretreatment. (Paper III).

| | Reference bleaching | | Alkali pre-treatment | | | |
|---|---|---|---|---|---|---|
| | Low chem | High chem | APT 2% NaOH | PPT 3% NaOH, 60 min | PPT 3% NaOH, 90 min | PPT 4% NaOH |
| SR number | 34 | 43 | 32 | 49 | 30 | 33 |
| Grammage (g/m$^2$) | 71.8 | 83.9 | 68.1 | 68.7 | 67.7 | 73.4 |
| Thickness (µm) | 112 | 113 | 109 | 107 | 107 | 103 |
| Apparent density (kg/m$^3$) | 639 | 743 | 627 | 644 | 684 | 657 |
| Bulk (m$^3$/kg) | 1.56 | 1.35 | 1.60 | 1.55 | 1.46 | 1.52 |
| Opacity (%) | 69.7 | 71.2 | 72.9 | 74.9 | 71.6 | 71.5 |
| Light scatter (m$^2$/kg) | 19.7 | 18.8 | 19.4 | 18.6 | 18.3 | 20.1 |
| Light absorption (m$^2$/kg) | 0.3 | 0.2 | 0.7 | 0.9 | 0.6 | 0.8 |
| Tensile index (Nm/g) | 63.9 | 69.8 | 52.9 | 53.5 | 57 | 56.8 |
| Tear index (Nm$^2$/kg) | 3.6 | 5.4 | 4.8 | 4.7 | 5.3 | 4.2 |

One option to decrease sodium hydroxide consumption in peroxide bleaching is to substitute it partially with sodium carbonate. Figure 8 illustrates the brightness development of the bleachings with partial alkali substitution of NaOH with $Na_2CO_3$ and the corresponding reference. The highest brightness was achieved with the 25% $Na_2CO_3$ share and it was equal to the reference pulp. Increasing the substitution to 40% the final brightness decreased only from 68% to 65% ISO. Sodium carbonate substitution increased the bleached yield slightly, but it may also impair the defibration if the degree of substitution is 40% or above (Paper III).

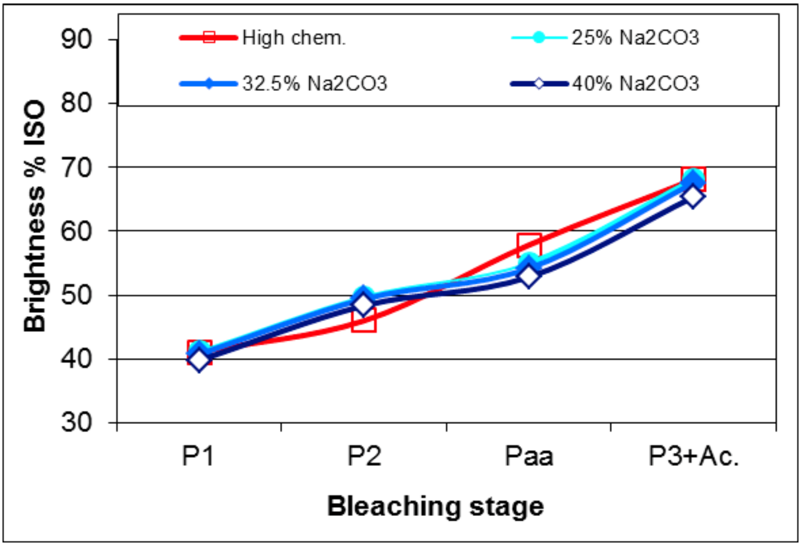

Figure 8. Brightness of sodium carbonate substitution bleachings and reference pulp after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching (Paper III).

Particularly in the first alkaline peroxide stage, a considerable amount of sugars are dissolved due to the high alkali charge in the stage. The role of these sugars, especially glucose and xylose, was studied by adding them in the first peroxide ($P_1$) stage (Paper III). The purpose of this was to test the hypothesis about their negative effect on bleachability. However, glucose addition in the $P_1$ stage clearly improved the pulp bleachability, since the final brightness was 2–5% ISO units higher than that of the reference pulp, Figure 9. Xylose addition arrived at the same final brightness as the reference pulp. The negative effect was not seen. This may result from the possible catalyst role of reducing sugars in alkaline peroxide bleaching (Heikkilä & Vuorinen 2000; Vuorinen & Heikkilä 2003). The yield of sugar addition bleaching trials was on a similar level to the yield of the comparable reference pulps. Sugar addition also did not have a significant effect on the technical properties of the paper. Xylose addition may impair the pulp drainability (Paper III).

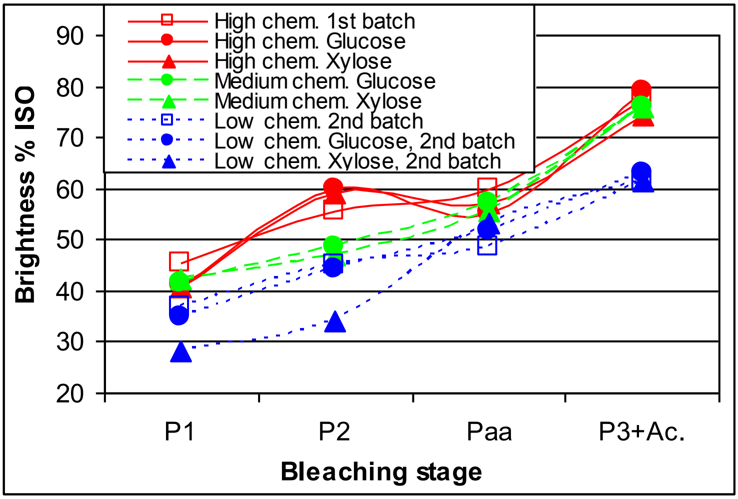

Figure 9. Brightness of sugar addition bleachings and reference pulp after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching. 1st batch = 07Straw air dried and stored in room temperature, 2nd batch = 07Straw stored in an unheated barn for about two years (Paper III).

The results (Paper III) showed that the minimization of sodium hydroxide consumption in the alkaline peroxide bleaching of the hot water treated wheat straw is challenging. However, the quality of produced pulp is satisfactory. If the final application does not require a high brightness level, this type of pulp may have several applications, such as for writing and printing papers and packaging materials.

### 4.1.2 Mechanical pulp for packaging

Non-wood pulping processes are typically chemical or chemi-mechanical processes (Paper I). Pure mechanical pulping has not been applied for nonwood materials. An option to simplify the defibration process including a hot water treatment and the following alkaline peroxide bleaching and reduce the chemical consumption could be a combination of mechanical refining with the hot water treatment. The produced, mechanical type of pulp could be used for packaging materials (Paper II, V). The easily dissolved solids are separated by hot water treatment and then the treated straw is mechanically refined and fractionated. The fibre fraction is used for packaging, the coarse fraction is returned to refining and fines, which hamper drainability, are removed and used in energy production. The formed fines and dissolved solids can be used for energy production, for instance for biogas production.

Mechanical refining of hot water treated wheat straw produces coarse fibre bundles (> 16 and > 30 mesh), fibres (< 100 mesh), broken fibre pieces (> 200 mesh) and fines (< 200 mesh). When increasing the refining time, the amount of the fibre bundles reduced and the amount of the fibres increased, as expected. When the coarse fraction was refined again the relative proportion of fibre fraction and coarse fines increased compared to the initial refining of straw, but still the amount of fine fines was not increased. Figure 10 shows the estimation of the fibre fractions analysed with Bauer McNett apparatus if the coarse fraction is returned to refining three times, assuming it is refined equally each time (Paper II).

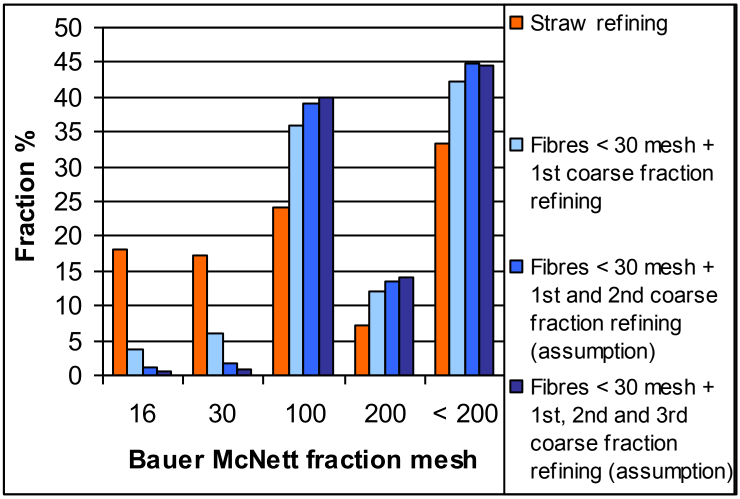

Figure 10. Mass balance of mechanically refined fibres. Estimation of coarse fibre fraction return to refining. Straw refining = fibre fractions, from refining of hot water treated straw, Fibres < 30 mesh = fibre fractions (< 30 mesh) including the sum fractions from previous refining(s) (Paper II).

The results from mechanical refining experiments (Paper II) suggest that it is possible to produce about 49% fibres for paper production and 41% of fines to be used in energy production. The amount of formed dissolved solids in the hot water treatment is about 10% at 120°C temperature. By altering the refining conditions it would be possible to increase the proportion outgoing to energy production.

The strength properties, especially the tensile strength, of the wheat straw pulp produced were very poor (below 5 Nm/g) while the drainability was good (Paper II). Scott Bond bonding strength was also relatively low (below 50 J/m$^2$). If the straw pulp was mixed with a pulp of better quality, the amount of straw pulp could be between 20% and 40% in the mix. The straw pulp amount was limited due to the strength properties; the tensile index limit was 30 Nm/g and the Scott Bond limit 100 J/m$^2$. The addition of wheat straw pulp impairs the surface and optical properties and thus the printability. This kind of wheat straw pulp with high bulk could perhaps be used as a raw material for the middle layer of a board when mixed with a pulp of better strength properties or for moulded fibre packages as such (Paper II).

The strength properties of the wheat straw pulps can be improved, for instance by sizing or by a chemical treatment such as a bleaching stage (Paper II) and thus increase the proportion of straw pulp in the mix. Another interesting option is to increase the hot water treatment temperature (Paper V). The preliminary results showed that if the hot water treatment and the following mechanical refining are performed at 170°C temperature, the amount of mechanical energy required for the defibration is significantly reduced. At the same time the properties of the pulp are clearly improved. The tensile index was 24.6 Nm/g and the Scott Bond 141 J/m$^2$ which are almost enough for the papermaking process (Paper V). By optimising the mechanical refining even better properties could be obtained.

The strength properties obtained can slightly be improved by a mild alkaline peroxide treatment. After the treatment, the tensile index of pulp was 30.1 Nm/g and Scott Bond 188 J/m$^2$. The yield loss in the hot water treatment stage was about 30%, see Figure 4. The amount of formed fines was approximately 25% of pulp. Part of the straw remained unrefined due to the mild refining conditions and wide gap between the blades. Thus the amount of fines would most probably increase 5–10% if the straw was totally defibrated (Paper V).

### 4.1.3 Dissolved solids and fines for energy

Lignocellulosics such as straw can be used as a raw material for ethanol production. Prior to the hydrolysis and fermentation, the straw is pretreated physicochemically to fractionate the lignocellulosic structure of the biomass and enhance the accessibility of cellulose (Montané et al. 1998). Typically, a steam explosion stage is used for fractionating the biomass prior to ethanol production. The fines and dissolved solids formed in the proposed pulping processes is suggested for use directly in ethanol production without a steam explosion if an ethanol plant was close to the pulp mill. If an ethanol plant was not close to the pulp mill, the better choice for energy production would be biogas production due to the small scale of the processes. Prior to biogas production, a hydrothermal pre-treatment enhance the biogas production (Kaparaju et al. 2009). The fines and dissolved solids formed in proposed processes could therefore also be used directly in biogas production (Paper V).

## 4.2 Chemical storage of wheat straw

The constant flow of high-quality raw material is essential to the mills' exploitation of annual plants. The non-wood raw material has to be stored for long periods because harvesting usually occurs just once a year. During storage, climate and moisture cause biological reactions, and the material easily decays. The whole year production may require massive ware houses to protect the raw material from climate. One option to guarantee quality raw material to the mills is to store it chemically at the farms prior to use (Paper IV).

### 4.2.1 Effect of chemicals on straw

Urea, formic acid and formic acid-based preservatives are commonly used chemicals on farms. The possibilities of these chemicals in the pre-treatment/chemical storage of wheat straw were studied (Paper IV). Urea is converted by the bacteria on straw to ammonia, which then acts to process the straw as an alkali (Butterworth 1985). The chemical treatment with alkalis softens the lignin structure (Butterworth 1985) and may modify the lignin-carbohydrate complex in straws, making the cellulose and hemicelluloses fractions more accessible. The urea pre-treatment darkened the straw due to the alkali darkening, but the formic acid pre-treatment did not have a significant effect on the straw colour (Paper IV).

Formic acid has an antibacterial effect due both to hydrogen ion concentration and to a selective bactericidal action of the undissociated acid (McDonald et al. 1991). Formic acid lowers the pH and thus limits fermentation and reduces the degradation of proteins to ammonia (McDonald et al. 1991). The effect of formic acid application on the chemical composition of silage varies according to the level applied, the dry matter content of the ensiled material and the species of crop (McDonald et al. 1991). When the dry matter content is higher, the effects of the preservative are lower. The changes in the chemical composition of the raw material are therefore assumed to be limited in the studied dry matter when the dry content is greater than 70% (Paper IV).

The chemical pre-treatment with formic acid or formic acid-based preservative did not change the chemical composition of wheat straws significantly (Paper IV). The total amount of sugars and gravimetric lignin seemed to be higher in the treated straws compared to the untreated straw. This higher organic content of the treated straws may be due to the dissolution/losses of ash and fines during the pre-treatment or the following washing stage. The chemical pre-treatment with formic acid or formic acid-based preservative may also loosen the straw structure and thus enhance the acid hydrolysis in the chemical composition analysis. The treatment with formic acid led to the lower pH of the pretreated straw which was seen as a lower pH of the first washing filtrate compared to the treatment with formic acid based preservative. The lower pH led to the lower ash content of the treated straws (Paper IV).

Morrison showed that formic acid silage decreased hemicelluloses content of ryegrass 10–20% but did not affect the lignin or cellulose content (Morrison 1979). In the case of lucerne silage the formic acid decreased the cellulose content but had less effect on the hemicelluloses fraction (Morrison 1988). He explained the results by the differences in the grass structures. The dry content of these wilted silages was not mentioned but it was probably much lower than that of the straw pre-treatments performed in Paper IV.

The bales treated with formic acid based preservative were not observed to be moulded by organoleptic evaluation even after 1.5 year time. This is an important factor in regard to occupational health of the raw-material handlers and their exposure to fungal particles. The reference bale without chemical pre-treatment was slightly mouldy after one year storage in an unheated barn. The bale expelled an excessive amount of small particles in the air during opening and also a mildew smell was observed, despite of the high dry matter content and shelter from the weather. However, the slight mould growth did not significantly affect the chemical composition of the straw compared to the corresponding frozen sample (Paper IV).

On the other hand, the outdoor storage in the field has been reported to have significant effects on the chemical composition of straw. Bicho and McRae (2004) exposed Canadian wheat straw to the weather for one year and discovered evidence of decay throughout the bales. The decay caused losses in the galactan, arabinan and ash contents, while the xylan level remained constant and lignin and glucan contents increased. These results concur with those of Collins et al. (1990), which indicate that water soluble components, such as ash and some water soluble polysaccharides, are rapidly leached from exposed straw.

### 4.2.2 Effect of chemical storage on pulping

The yield loss of chemical pre-treatment with urea or formic acid was practically compensated for in hot water treatment. The bleached yield was also almost the same for pretreated and reference pulp (Paper IV). The brightness of hot-water-treated and bleached pulp was affected by the pre-treatment chemical and time. After 2–6 months of pre-treatment time, the pulp brightness was clearly lower, as can be seen in Figure 11. The decline in brightness in the case of formic acid treatment may be due to the lignin structure alteration caused by the acid addition (Leschinsky et al. 2008; Shiming & Lundquist 2000).

Urea pre-treatment reduced the brightness of hot water treated and peroxide bleached pulp even more (Paper IV). The colour difference was already visible in the pretreated straws. The darkening in the pretreated straws derives from the alkali darkening. The urea is converted to ammonia during the pre-treatment, which then forms ammonium with water. The balance of ammonia and ammonium ions is transferred to ammonia when hydroxide ions are added in an alkaline peroxide stage. A part of the added hydroxide is consumed in this side reaction instead of the actual bleaching reaction, thus impairing the bleachability (Paper IV).

After about nine months of storage, the bleachability of pretreated straw with both formic acid and urea was clearly improved. The better bleachability may be due to the loosened structure of wheat straw or lignin alteration. Furthermore the dissolution of sugars during the pre-treatment or the hot water treatment may have a positive effect on the bleachability (Paper III). The addition of glucose or xylose to the first peroxide stage of a P-P-Paa-P bleaching sequence for hot water-treated wheat straw improved the pulp bleachability (Paper IV).

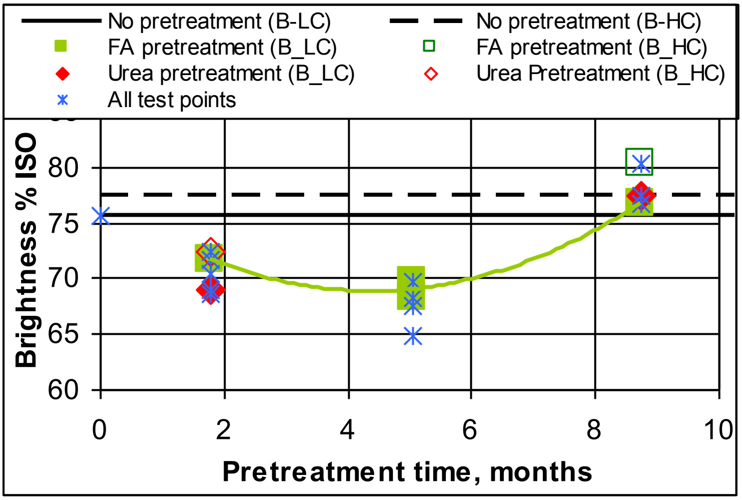

Figure 11. Final brightness as a function of straw pre-treatment time. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. P = alkaline peroxide stage, Paa = peracetic acid stage. Pre-treatment in Plexiglas acrylic silos. FA = Formic acid. B-LC = lower bleaching consistency (< 10%), B-HC = higher bleaching consistency (10%) (Paper IV).

The results of straws treated with formic acid based preservative from round bale experiments showed a similar trend in the final brightness of hot water treated and peroxide bleached wheat straw pulp (Figure 12). First the brightness decreased, but turned to increase after the nine months pre-treatment time. The change appeared after longer pre-treatment time compared to the laboratory scale silo experiments. This may be due to the storage temperature: the round bales were stored in an unheated barn where the temperature was clearly lower compared to the silo experiments at room temperature (Paper IV). The straw in round bale trials was still totally usable after 1.5 year and the pre-treatment time could probably even be prolonged if needed. The bleachability of the reference straw, stored in an unheated barn, impaired during 1.5-year storage time, even though the raw material was sheltered from the sun and moisture, see Figure 12.

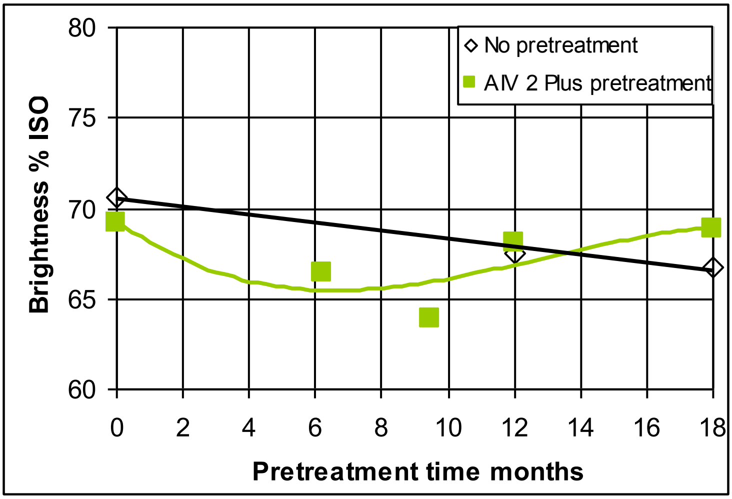

Figure 12. Final brightness as a function of straw pre-treatment time. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. Pre-treatment in round bales. Reference bales (no pre-treatment) stored in an unheated barn.

It is possible to combine a chemical pre-treatment/storing stage also with a soda cooking process, especially if the pre-treatment is performed with formic acid (Figure 13). Urea treatment has a negative effect on the delignification due to the consumption of hydroxide ions in the side reaction of ammonium and hydroxide to ammonia. This observation suggests that the storage of straw with sodium hydroxide could be one possibility to ensure high-quality raw material to soda pulp mills and even reduce the cooking chemical consumption (Paper IV).

These results show that a chemical pre-treatment stage/storing of straw or even other non-woods can be integrated with an existing pulping process. The chemical storing can ensure more homogenous raw material resources throughout the year or even longer. Furthermore, no large storing houses are required; hence the straws can be stored on farms with existing equipment. The storage of chemically pretreated straw could also be integrated with energy processes or other processes utilising non-woods as a raw-material. The uniform raw material is a relevant issue to these mills as well. Formic acid is a potential preservative, but other formic acid based preservatives such as AIV 2 Plus could also be used if available on farms (Paper IV).

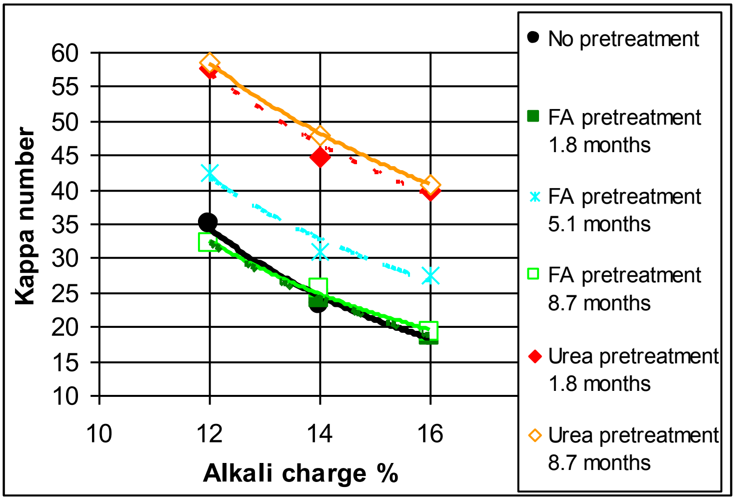

Figure 13. Kappa number as a function of straw pre-treatment time. Soda cooking at 160°C for 60 min. Pre-treatment in Plexiglas® acrylic silos (Paper IV).

## 4.3 Markets and driving forces

### 4.3.1 China

In 2006–2009 the government of China closed hundreds of non-wood pulp and paper mills, equal to an estimated 6.5 million tonnes of total annual capacity. The aim of these shutdowns has been to reduce pollution and modernise the industry. By the end of 2010, more than 4.32 million tonnes of annual non-wood pulp and paper mill capacity shutdowns are targeted. If China reaches its target, the total estimated annual capacity closures will rise to 10.82 million tonnes (Smith 2010).

China has limited supply of wood. Therefore, the demand for non-wood pulp is not decreasing even though the small and polluting mills are closed, see Figure 14 (Kuusisto 2010). The production of the small mills is suggested to be substituted by larger mills, see Figure 14 (Kuusisto 2010) such as Chempolis. An alternative could be if the small mills were replaced by other small mills with simple and environmental safe process such as suggested in this work. The existing logistics of raw material support the latter proposal.

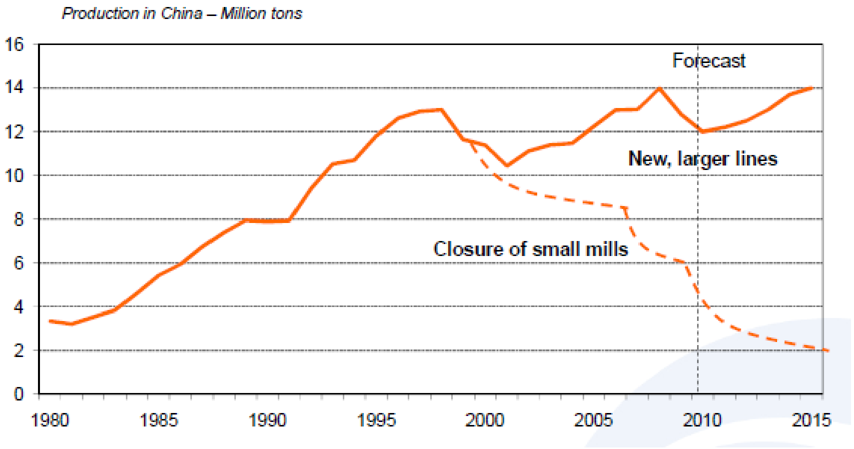

Figure 14. Future of non-wood pulp in China (Kuusisto 2010).

The bioenergy boom is increasing in China due to the pressure of carbon emissions reduction. Recently, Chinese policies have announced targets for bioenergy and also additional finance is addressed for renewable energy development using clean development mechanism (Wang & Chen 2010).

### 4.3.2 Europe

One of the key megatrends of the European pulp and paper industry are market saturation, overcapacity and increasing competition, which have weakened the profitability in the traditional business areas, and caused the production shifts from mature to emerging markets. At the same time, the availability of fibre raw material wood has become significantly scarcer (Pöyry 2010).

Exceptionally mild winters and shorter frost periods have caused difficulties in wood harvesting and transport and the implementation of round wood export tax has restricted the wood supply from Russia. This has led to the shortage of fibre raw material. At the same time, the demand for biomaterials has increased due to the international agreements on sustainable development. In addition, the demand for recovered paper has increased.

Recovered paper prices have shown an increasing trend, see Figure 15. The main drivers behind this are increasing demand for the production of recycled fibre based papers and paperboards, production economics in papermaking and energy production, administrative/institutional actions (legal actions, local and international agreements, recycling targets), and increasing collection rates implying higher marginal costs of collection, which will eventually lead to rising trend prices. In the past, the use of recovered paper has been justified on cost grounds – now that the tide is turning and recovered paper is becoming gradually more expensive, non-wood pulps could regain their lost position in selected applications.

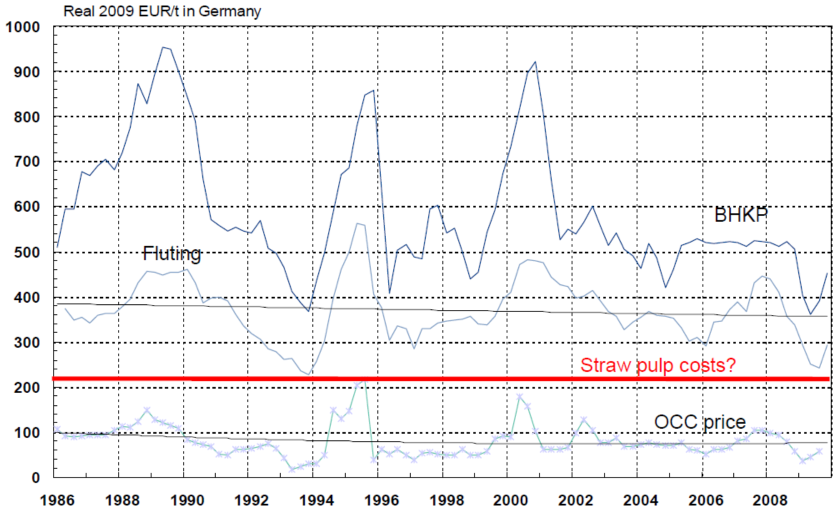

Figure 15. Real Price Development of old corrugated container (OCC) and bleached hardwood kraft pulp (BHKP) 1986–2009 (Pöyry 2010).

Recycled paper and non-wood pulp could even have synergy effects due to the different paper properties. The lower quality material could be used for energy production and the smallish units would suit for local and flexible fibre and energy production where the logistics of raw material would be solvable. In addition the produced straw fibres could be used in other applications such as biocomposites in the future. Furthermore, non-wood raw material, such as straw, is widely available in Europe as a by-product from food production.

The European Union is committed to control climate change and to improving the security of its energy supply. According to the new Directive on renewable energy, a 20% share of total energy will be from renewable sources by 2020. Bioenergy represents more than two-thirds of the total renewable energy in the EU. The main sources are forestry with half of the EU's renewable energy, agriculture and organic waste. The share of agriculture is growing fast (Summa 2008, EU 2010).

The boom in bioenergy will most probably increase the amount of non-wood raw material in the market. At the same time increasing demand for packaging materials in the European Union could open possibilities for local and flexible fibre and energy production from annual plants that could be applied in a small scale.

### 4.3.3 Assessment of suggested processes

The potential of the suggested processes were evaluated and compared to soda pulp and ethanol production. The processes were limited to the incoming straw amount of 100,000 BD t/a due to the favourable logistics distance. The investment and production costs highly depend on the local conditions and the equipment selected. Furthermore, the prices of products depend on the market situation and especially on the demand for the product in question. Therefore the aim of the evaluation was to determine the potential of the processes (Paper V).

The traditional bioethanol production from straw is not profitable due to the high investment and production costs (von Weymarn 2007), unless the price of produced bioethanol would be significantly higher than the price of the Brazilian sugarcane ethanol. The combined production of fibres and energy by the suggested "mechanical" approach has significantly lower investment costs than the soda process or the bioethanol plant. However, the value of produced unbleached pulp is lower than the value of bleached pulp. The biogas production compensates the lower pulp price; hence the process seems to have potential for further investigation, especially if the bioenergy production is promoted with higher prices in some EU countries. The advantage of the "chemical" approach is the clearly higher pulp yield which increases the income from the pulp. However, at the current stage the process consumes high amounts of chemicals which significantly increase the production costs and environmental impact. (Paper V).

In China, the combined straw pulp and energy production seem to have possibilities due to the chronic fibre shortage and also the increasing demand for bioenergy. The suggested "mechanical" process option could be integrated with containerboard production.

In Europe, the possibilities for combined straw pulp and energy production seem to be limited unless the price of recycled paper increases above EUR 200 per ADt or significant subsidies are made to encourage bioenergy production. Then the mills which would most benefit from cheaper raw material are the small containerboard mills with a risk of running out when demand decreases. The maximum market potential of straw pulp in Europe is suggested to be about 3 million tonnes/a in the fluting production, assuming that 30% of the fluting furnish could be replaced by straw pulp. This would mean 60 mills with 50,000 ADt/a production.

# 5. Concluding remarks

Wheat straw is a potential raw material source for combined fibre and energy production in a small scale. In China, a steady demand for non-wood fibres exists. The modernisation of non-wood pulping industry and the lack of wood raw material offer possibilities for straw pulp produced by simple practice if the process is economically competitive. In Europe, the utilisation of non-wood fibres would be established only if it was combined with energy production since the demand for renewable energy is increasing but the demand for fine papers is declining.

Wheat straw pulp can be produced by hot water treatment and following chemical or mechanical defibration. The "mechanical" approach produced pulp for packaging materials. The dissolved solids and fines which hamper drainability can be utilised for energy such as biogas production. The low pulp properties can be improved by increasing the hot water treatment and mechanical refining temperature or by mixing the pulp with a pulp of better quality. In addition, a chemical treatment such as alkaline peroxide stage or sizing slightly improved the pulp properties. Silica is not a problem in the suggested process since the chemical consumption is low and a recovery system is not required. The most suitable paper product area for unbleached straw pulp is fluting in the containerboard product area.

The "chemical" approach produced pulp for printing and writing or cartonboards with FBB and WLC. The minimisation of the chemical consumption in the alkaline peroxide bleaching appeared to be challenging indicating that a chemical recovery system would be needed unless the brightness target 75% ISO can be reduced. In that case, silica may cause problems. However, the obtained pulp properties were relatively good and the benefit is a significantly higher yield than that of a soda process.

One of the main problems associated with utilising straw as a fibre raw material is the availability of quality raw material throughout the year. The straw easily decays when exposed to moisture and heat during storage between the harvesting times. It was shown that wheat straw can be stored chemically with formic acid based chemicals over a year without significant changes in the chemical composition. The chemical storage can be integrated with suggested chemical or mechanical defibration, soda pulping process or any other process utilising non-wood fibres.

The costs of the processes highly depend on the local conditions and the equipment selected. The preliminary assessment showed that the investment costs of the “mechanical” approach are clearly lower than those of a soda process or an ethanol plant. In addition, energy production such as biogas improves the profitability of the process. Bioethanol production at the current prices is not profitable. It seems that the combined fibre and energy production is more cost effective, but highly depends on the prevailing markets. In Europe, the possibilities for combined straw pulp and energy production seem to be limited on the grounds of pulp market volumes. If the produced pulp competes with recycled fibres in the final application, the price of recycled paper should rise above EUR 200/ADt or significant subsidies should be made to encourage bioenergy production to make the straw pulp process economically viable.

The fundamental principle of this work was to develop a cost-effective process producing adequate quality pulp from wheat straw for present paper or paperboard products. If the prospect changes in the future, the wide range of non-wood fibres and their properties could still offer a solution for instance to biocomposites.

Further research is needed for optimising mechanical refining at high temperature and the refiner configuration developed. In addition, the chemical storage of wheat straw and other non-wood raw materials must be optimised. Pilot scale trials would give a solid basis for more accurate feasibility studies. Furthermore, the suitability of produced straw fibres for biocomposites must be examined.

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Paper I

# Non-wood pulping possibilities – a challenge for the chemical pulping industry

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# Non-wood pulping possibilities – a challenge for the chemical pulping industry

**ANJA LEPONIEMI**[1]

## SUMMARY

Chemical pulping processes that are currently used for pulping non-woods are mainly based on those adapted from the pulping of wood. Several newer methods, still at the laboratory or pilot scale, have also been announced. This paper reviews the current status of chemical and chemi-mechanical non-wood pulping processes, and describes their advantages and disadvantages. The review is based on claims made in the literature and is aimed at assisting researchers in their preparation for the development of a small scale, competitive process that could be a part of a complete utilisation chain for annual plants. Overall it can be concluded that the chemical composition and/or the special features of the non-wood raw materials have so far not been fully exploited.

## INTRODUCTION

Annual plants and forests of the world are of course our largest source of fibre. Table 1 presents the areas of arable land and permanent meadows alongside the major areas of forest cover in major regions of the world. The total area of arable land and permanent meadow is 4.8 billion hectares while the total area of forest is only just below 4 billion hectares. Moreover the area of forest is unevenly distributed (*1*).

**KEYWORDS**
Non-wood fibre, annual plants, pulping processes, review, soda, organosolv, ethanol, methanol, formic acid, acetic acid, chemi-mechanical process, mild acid cooking

Agro-fibres have been utilised industrially for many years in both energy production and for paper manufacturing, particularly in China and India. However the widespread utilisation of annual plants in pulping has not been technically or economically attractive in western countries due to the lack of a simple and environmentally efficient pulping method. World pulp production in the year 2004 was 193 million tonnes of which only 17 million tonnes (9%) was non-wood based pulp, Table 2 (*2*).

It can be concluded that annual plants are a remarkable and under-utilised potential fibre resource. Any competitive pulping method utilising annual plants as a paper making raw material could be a part of the whole chain utilisation of agro-fibres. In such a scheme the most valuable fraction would be used for human or animal food or commodity production, the second suitable fraction of the plant would be utilised as a raw material in traditional paper making, and the low value fraction (and the eventual non recyclable waste papers) then utilised directly in energy production in the form of for instance solid waste fuel briquettes.

The benefits of plants as a fibre resource are their fast annual growth (*4*) and the smaller amount of lignin binding their fibres together (*5*). Table 3 presents the average annual yields of some paper-making raw materials. Table 4 presents the average fibre dimensions and chemical composition respectively. Another benefit is that non-wood pulp can be produced at low temperatures with lower chemical charges. In addition smaller mill

**Table 1**
**The area of arable land and permanent meadows in year 2003 versus the area of forest in year 2005**

| | Area of arable land and permanent meadows year 2003 (million hectares) | Forest area year 2005 (million hectares) |
|---|---|---|
| EUROPEAN UNION (25 countries) | 164 | 146 |
| EUROPE | 467 | 1001 |
| NORTH AMERICA | 469 | 677 |
| SOUTH AMERICA | 571 | 832 |
| ASIA | 1617 | 572 |
| - China | 543 | 197 |
| - India | 172 | 68 |
| AFRICA | 1120 | 635 |
| OCEANIA | 456 | 206 |
| WORLD | 4835 | 3952 |
| References | (*3*) | (*1*) |

**Table 2**
**Non-wood pulp and wood pulp production in year 2004 (*2*)**

| | Non-wood Pulp Production (million tons) | Wood Pulp Production (million tons) | Non-wood pulp production of total pulp production (%) |
|---|---|---|---|
| EUROPEAN UNION (25 countries) | 0.59 | 39.6 | 1.5 |
| EUROPE | 0.64 | 50.0 | 1.3 |
| NORTH AMERICA | 0.29 | 80.9 | 0.4 |
| SOUTH AMERICA | 0.39 | 14.1 | 2.7 |
| ASIA | 15.52 | 24.7 | 38.6 |
| - China | 12.15 | 4.1 | 74.9 |
| - India | 1.85 | 1.8 | 50.4 |
| AFRICA | 0.35 | 2.7 | 11.5 |
| OCEANIA | 0.00 | 2.7 | 0.0 |
| WORLD | 17.4 | 175.4 | 9.0 |

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**Table 3**
**Average annual yields of different papermaking raw materials (*4*)**

| Plant | Fibre yield tonnes/year/ha | Pulp yield tonnes/year/ha |
|---|---|---|
| Wheat straw | 4 | 1.9 |
| Rice straw | 3 | 1.2 |
| Bagasse | 9 | 4.2 |
| Bamboo | 4 | 1.6 |
| Kenaf | 15 | 6.5 |
| Hemp | 15 | 6.7 |
| Elephant grass | 12 | 5.7 |
| Canary grass | 8 | 4.0 |
| Scandinavian softwood | 1.5 | 0.7 |
| Fast-growing softwood | 8.6 | 4 |
| Temperate softwood | 3.4 | 1.7 |
| Fast-growing hardwood | 15 | 7.4 |

**Table 4**
**Fibre dimensions and chemical properties of some papermaking raw materials (Adapted from (*5*))**

| Plant species | Average fibre length mm | Average diameter µm | L/D ratio | Alpha Cellulose | Lignin % | Pentosans % | Ash % | Silica % |
|---|---|---|---|---|---|---|---|---|
| Wheat straw | 1.48 | 13 | 110:1 | 29-35 | 16-21 | 26-32 | 4-9 | 3-7 |
| Rice straw | 1.41 | 8 | 175:1 | 28-36 | 12-16 | 23-28 | 15-20 | 9-14 |
| Bagasse | 1.70 | 20 | 85:1 | 32-44 | 19-24 | 27-32 | 1.5-5 | 0.7-3 |
| Bamboo | 1.36-4.03 | 8-30 | 135-175:1 | 26-43 | 21-31 | 15-26 | 1.7-5 | 1.5-3 |
| Kenaf, bast fibres | 2.74 | 20 | 135:1 | 31-39 | 15-18 | 21-23 | 2-5 | |
| Kenaf, core fibres | 0.60 | 20 | 20:1 | 34 | 17.5 | 19.3 | 2.5 | |
| Hemp, bast fibres | 20 | 22 | 1000:1 | 55-65 | 2-4 | 4-7 | 5-7 | <1 |
| Hemp, core fibres | 0.51 | 31 | 16: | 39-49 | 16-23 | 16-23 | 3-4.5 | <1 |
| Oilseed flax | 27 | 22 | 1250:1 | 34 | 23 | 25 | 2-5 | |
| Common reed | 1.50 | 20 | 75:1 | 45 | 22 | 20 | 3 | 2 |
| Coniferous trees | 3.00 | 30 | 100:1 | 40-45 | 26-34 | 7-14 | 1 | <1 |
| Deciduous trees | 1.25 | 25 | 50:1 | 38-49 | 23-30 | 19-26 | 1 | <1 |

sizes can be economically viable, given a simplified process. Non-wood pulps are also more easily refined. From the farmer's point of view, non-food applications can give additional income to that from food crops or cattle production.

Several disadvantages of using annual plants have been reported. The problems of the separation of valuable parts of the raw-materials and those of logistics are of central importance. The harvest time for annual crops is also short and the fibre losses during collection high. Beside these issues the plants usually have a high silica content, which presents many problems particularly in chemical recovery systems (*6*). Indeed, many small non-wood pulp mills have no chemical recovery systems at all causing excessive local environmental impacts. Finally the poor drainage rates from non-wood pulps can result in low papermaking production rates.

This paper reviews the more recent developments in chemical and chemi-mechanical non-wood pulping processes and the advantages and the disadvantages of these systems. The review relies heavily on the accuracy of reports in the literature and is a necessary first step to assist in the development of a novel, simple and ecologically safe delignification method for annual plants.

Other reviews of non-wood pulping have also recently been published. For instance Siegle has published a review of current developments in formic acid pulping (*7*) and Hammet et al. have published a review of non-wood as an alternative to wood fibre in China's pulp and paper industry (*8*).

Alkaline cooking methods for non-wood materials have typically been adapted from processes for the delignification of wood raw materials. The first section therefore discusses alkaline methods in general, where sodium hydroxide or sodium carbonate is used as a cooking chemical. The alkaline sulphite process is described in the section "Sulphite processes". The processes using solvents, for instance methanol or ethanol, are discussed in the section "Organosolv processes".

## ALKALINE COOKING METHODS

The main problem of alkaline processes for pulping of non-wood fibres is that silicates in non-wood plants dissolve into the liquor during cooking. The presence of silicate ions causes serious problems in chemical recovery systems such as scaling on heat transfer surfaces in evaporators, high viscosities of concentrated liquors and also problems in caustisizing. The high viscosity of concentrated liquors has a subsequent negative influence on both evaporation and combustion processes (*6*).

Attempts to address these problems via desilication methods can be divided into three categories. Firstly, lowering black liquor pH by acid flue gases or by pure carbon dioxide causes the silicate ions and some of the organics to agglomerate and the solidified matter can then be separated from the liquor by filtration or centrifuging. Secondly, silica can be precipitated onto pulp as insoluble silicates by the addition of metal cations such as $Al^{3+}$, $Ca^{2+}$ and $Mg^{2+}$. Lastly, other methods such as presilication of the raw material can be used. However, none of these methods completely overcome the silica problem (*6*). Hence many non-wood mills, for instance in China or India, have no recovery system at all and the effluents are discharged to rivers without treatment in many cases.

Table 5 presents data from the literature on a selection of pulping conditions and resultant pulp properties for alkaline cooking methods. The average kappa number of unbleached alkaline pulps is 10-20 and unbleached pulp yields are 45-50%, except for the semi-chemical SAICA process, where the pulp yield is over 60%.

### Soda processes

The soda pulping process for non-wood material is widely applied all over the world. The cooking chemical is mainly sodium hydroxide and the amount needed depends on the particular fibre raw material. The cooking temperature also depends on the cooking time and alkali charge. Typical NaOH charge is around 16% and cooking temperature 140-170°C (*10,11,14-16*).

**Table 5**
**Alkaline cooking conditions and pulp properties**

| **Process**<br>**Raw Material** | **Kraft (mill)**<br>**Reed canary grass** | **Soda**<br>**Bagasse** | **Soda-AQ**<br>**Bagasse** | **Soda**<br>**Wheat straw** | **Soda-AQ**<br>**Wheat straw** | **Soda-Oxygen**<br>**Wheat straw** | **NACO**<br>**Bagasse** | **NACO**<br>**Wheat straw** | **SAICA**<br>**Wheat straw** |
|---|---|---|---|---|---|---|---|---|---|
| Effective alkali charge % (as NaOH) | 14.0 | 12.0 | 12.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 6.5-8.5 |
| Sulphidity % | 35.0 | - | - | - | - | - | - | - | - |
| AQ % | - | - | 0.1 | - | 0.1 | - | - | - | - |
| Temperature °C | 160 | 165 | 165 | 140 | 140 | 140 | 135 | 130 | 94-97 |
| Time min | 10 | 60 | 60 | 60 | 60 | 60 | 75 | 60 | 150-210 |
| Oxygen pressure bar | - | - | - | - | - | 8 | 6 | 6 | - |
| Kappa number | 9.3 | 21.5 | 13.3 | 20.9 | 18.6 | 18.4 | 14.4 | 14.0 | |
| Yield % | 54.0 | 53.6 | 50.5 | | | | 48.4 | 42.1 | 67.1 |
| Screened yield % | | 50.1 | 49.3 | 45.0 | 50.0 | 46.2 | | | |
| SR number | 21 | | | | | | 40 | 40 | |
| Tensile index N.m/g | 49.1 | | | | | | 62 | 69 | |
| Burst index kPa.m$^2$/g | | | | 5.0 | 5.4 | 3.5 | 4.0 | 4.2 | |
| Tear index mN.m$^2$/g | 7.8 | | | 3.9 | 3.7 | 6.0 | 4.0 | 3.5 | |
| Brightness % ISO | 45.8 | 25.6 | 37.2 | 49.0 | 53.1 | 57.8 | 48.0 | 42.0 | |
| Reference | *(9)* | *(10)* | *(10)* | *(11)* | *(11)* | *(11)* | *(12)* | *(12)* | *(13)* |

The advantage of soda cooking compared to kraft cooking is the absence of sulphur. This avoids the generation of malodorous cooking gases and simplifies the recovery boiler construction (*17*).

The soda process can be improved by adding anthraquinone (AQ) or oxygen or both during cooking. AQ accelerates the cooking and protects the carbohydrates, so that lower kappa numbers are obtained with the same cooking conditions compared to non-AQ soda cooking. At the same time the pulp yield remains high (*10*). Khristova et al. have reported that the addition of AQ in soda cooking of kenaf accelerates delignification, reduces alkali consumption, kappa number and pulp rejects, increases pulp brightness, yield and viscosity, and gives pulps with properties superior to those from reference soda pulping (*18*).

The use of oxygen increases the delignification rate in soda cooking (*11*). The addition of anthraquinone to the soda-oxygen process further improves the pulp yield and physical properties. An interesting feature of soda-oxygen cooking is that the main portion of the dissolved silica precipitates on the fibres instead of remaining dissolved in the cooking liquor. Up to 96.5% of the silica in the raw materials can be precipitated on fibres as kaolin by adding 3% aluminium oxide ($Al_2O_3$) to soda-oxygen pulping (*11*).

Precipitation of silica is dependent on the pH of the cooking liquor. Okayama and Li noticed that in soda and soda-oxygen cooking, if the pH drops from 11.3 to 10.2, reprecipitation of silica increased dramatically from about 10% to 90% (*16*).

### NACO process

The NACO process is a variation of soda oxygen pulping. Straw pulp has been produced in full-scale mill operations using this process. The principal idea of the NACO process involves oxygen delignification to low kappa number in a sodium carbonate solution, with some sodium hydroxide as an activating and make-up chemical (*12,19*). Oxygen delignification takes place in a special reactor, a so-called pressurised, continuous turbopulper. The turbopulper has a perforated plate and rotor arrangement in the base that extracts cooked fibre out of the reactor. Typically, two turbopulpers are used in series operating at 6-7 bar pressure, with a pulp consistency of 8% (*20*).

The NACO process involves pre-treatment of straw, delignification, bleaching, incineration and chemical recovery. First the raw material is pre-treated at 50°C with a small amount of alkali (1-2% NaOH) and mechanical action. The main aims of this pre-treatment step are to remove heavy contaminants, to reduce silica content of the raw material and to wash out waxes from the straw which would inhibit subsequent chemical impregnation in the delignification stage. With such pre-treatment it is possible to obtain a 50% reduction of the silica in the raw materials (*12,19*).

The turbopulper is used in the main delignification stage. Delignification takes place at 130-145°C depending on the raw material used. The $Na_2CO_3$ charge also depends on the raw material and is typically around 20-25%. Oxygen pressure is at the same level as in the oxygen delignification stages used for wood pulp. An addition of 5-10% NaOH to the delignification stage improves the efficiency (*19*).

## SAICA process

The SAICA process is a semi-chemical pulping method using sodium hydroxide as the cooking chemical. Chopped and cleaned wheat straw - obtained by hammer milling and pneumatic dry cleaning - is impregnated with black liquor in the hopper. Impregnated straw is fed to a continuous indirectly heated digester, which operates at 94-97°C and atmospheric pressure. Pre-impregnation (with spent cooking liquor) helps the straw to absorb the fresh cooking liquor and increases its specific weight which improves feeding conditions. It also permits the utilisation of any active chemicals that are residual in the spent liquor (*13*).

Cooking takes from 2 to 4 hours at 94-97°C and atmospheric pressure. The digester is slightly inclined and two counter-rotating screws transport the straw upwards as liquor moves downwards. NaOH is added at the intermediate point of the digester, while water is added near the discharge zone, providing washing. The black liquor is continuously extracted from the lowest point of the digester and partially washed straw is removed at the top. Part of the black liquor is recycled to pre-impregnate the raw straw. The semi-chemical pulp obtained is washed and refined and is typically used in corrugating paper manufacture (*13*).

**Table 6**
**Sulphite pulping conditions and pulp properties**

| **Process**<br>**Raw Material** | **Neutral sulphite Wheat Straw** | **Neutral sulphite Wheat Straw** | **Neutral sulphite Wheat Straw** | **Neutral sulphite Wheat Straw** | **Neutral sulphite Wheat Straw** | **Neutral sulphite Wheat Straw** | **Alkaline sulphite Bagasse** |
|---|---|---|---|---|---|---|---|
| $Na_2SO_3$ charge % | 8.0 | 8.0 | 12.0 | 12.0 | 15.0 | 15.0 | 18.0 |
| $Na_2CO_3$ charge % | 1.7 | 1.7 | 2.6 | 2.6 | 3.2 | 3.2 | |
| NaOH charge % | | | | | | | 3.0 |
| Temperature °C | 165 | 165 | 165 | 165 | 165 | 165 | 160 |
| Time min | 30 | 90 | 30 | 90 | 30 | 90 | 60 |
| Kappa number | 18.6 | 18.8 | 17.2 | 14.5 | 15.9 | 12.8 | 9.7 |
| Yield % | 71.3 | 64.7 | 62.4 | 61.4 | 61.8 | 55.0 | 63.9 |
| SR number | 48.0 | 39.0 | 26.0 | 24.0 | 33.0 | 20.0 | |
| Tensile index N.m/g | 25.9 | 38.2 | 38.3 | 51.2 | 58.6 | 52.0 | |
| Burst index kPa.$m^2$/g | 1.2 | 1.9 | 1.8 | 2.2 | 2.6 | 2.3 | |
| Tear index mN.$m^2$/g | 2.2 | 3.4 | 3.9 | 4.3 | 5.6 | 4.3 | |
| Brightness % ISO | 26.4 | 28.8 | 34.6 | 39.7 | 37.3 | 42.3 | 52.6 |
| Reference | (*25*) | (*25*) | (*25*) | (*25*) | (*25*) | (*25*) | (*26*) |

The rest of the black liquor is sent to effluent treatment but the lignin in it could be separated by precipitation with acid or carbon dioxide and then filtered and washed. Lignin separated in such a way is clean, sulphur-free. Most of the silica remains in the filtrate. After lignin separation the filtrate is treated biologically. Alternatively, oxygen-based wet oxidation of the filtrate can be used to generate energy and green liquor. Silica is removed from the green liquor before causticizing (*13*).

### Kraft process

The kraft method is the dominant process used for chemical pulp manufacture from wood, but it is not as common in non-wood pulping (*17*). Most of the world's non-wood pulp mills produce less than 5000 t/year and there are only 11 mills in the world producing 100 000 t or more non-wood pulp (*21*). Issues with the local availability of non-wood raw material reduce the optimum size of the pulp mills making the kraft process, which is really only competitive at large throughput, less cost-effective for non-wood pulp mills (*22*).

The strength properties of non-wood kraft pulps are not particularly superior to those of soda pulps and it brings odour problems (*17*)

### Lime based processes

The semi-chemical lime process is one of the oldest processes for the production of corrugating medium and yellow straw board (*23*). No recent research data on lime processes has been published, therefore the process is not discussed further in this review.

## SULPHITE PROCESSES

This section discusses neutral and alkaline sulphite processes. Other alkaline sulphite processes using methanol or ethanol are discussed in the section "Organosolv processes". Magnesium bisulphite and ammonium bisulphite pulping is still carried out in some mills in China, but current research is directed towards more advanced processes (*24*). Table 6 presents a range of pulping conditions and pulp properties of neutral and alkaline sulphite cooking methods from the literature. The average kappa number of unbleached sulphite pulps is 10-20 and unbleached pulp yield is 55-70%.

### Neutral sulphite process

The active chemical in the neutral sulphite process (NS) is sodium sulphite, which is produced by dissolving sulphur dioxide in sodium carbonate. The sodium carbonate residual in the cooking liquor buffers the pH in the range 7-8. According to Ali et al (*25*) the sodium sulphite dosage is 10-15% for bleachable grades of wheat straw pulp, the cooking temperature is 165°C, yield is 8-10% higher and the pulp is easier to bleach than comparable soda pulps. These laboratory experiments do not, however, clarify where the silica from the raw material is located after cooking.

Anthraquinone (AQ) can also be used as an additive in the neutral sulphite process (NS-AQ). The application of NS-AQ process results in a reduction in the amount of organics in the spent liquor and produces a "kraft-like" pulp at a higher yield. Recirculation of the spent liquor however decreases delignification and impairs pulp yield and quality (*27*).

A high yield pulp, with low kappa number, can be achieved in the pulping of rice straw by the use of the neutral sulphite semi-chemical (NSSC) process. The pulp has good opacity and strength but a low tear factor. The kappa number of the rejects is similar to the kappa number of the accept pulp, therefore the rejects can be re-refined and added back to the pulp. The yield in the NSSC process is about 65% at kappa number of 11. The addition of a sodium carbonate or sodium hydroxide buffer reduces the yield to 62% and kappa number to 7.5. Short cooking times of 30 min result in yields of about 80% and kappa numbers of about 20 (*28*). Some mills in China use the NSSC process with rice straw for containerboard production (*29*).

### Alkaline sulphite process

Alkaline sulphite (AS) cooking refers to a cooking process using cooking liquor made up of NaOH and $Na_2SO_3$ with a cooking pH of 10-13.5. The advantage of the AS process compared to the kraft process is the absence of malodorous gases. The use of anthraquinone in alkaline sulphite (AS-AQ) pulping provides higher yield and higher viscosity at a given kappa number (*30*).

Much research on AS-AQ pulping of straw materials has been carried out in China, showing that, under the same cooking conditions, the selectivity of delignification and pulp yield increases when sulphite concentration increases. For wheat straw pulping the optimum sulphite concentration in the cooking liquor is 0.3-0.5 (*31*). With kenaf bark, yield,

**Table 7**
**Pulping conditions and pulp properties of alcohol cooking methods**

| Process<br>Raw material | ASAM<br>Bagasse | Free Fiber<br>Wheat straw | ASAE<br>Wheat straw | ASAE<br>Wheat straw | ASAE<br>Wheat straw | ALCELL<br>Reed | ALCELL<br>Straw | ALCELL<br>Kenaf | IDE<br>Reed |
|---|---|---|---|---|---|---|---|---|---|
| $Na_2SO_3$ charge % | 16-18 | - | 12.0 | 14 | 16 | - | - | - | - |
| Alkali ratio | 0.7 | - | | | | - | - | - | - |
| NaOH charge % | | $Na_2CO_3$ | 3 | 3.5 | 4 | - | - | - | $Na_2CO_3$ |
| AQ % | - | - | 0.1 | 0.1 | 0.1 | - | - | - | 0.022 |
| Methanol / Ethanol % | 15-20 * | methanol gas phase | 50 | 50 | 50 | ~ 50 | ~ 51 | 60 | 50% |
| Cooking temperature °C | | | 170 | 170 | 170 | 195 | | 200 | |
| Kappa number | 3-6 | 10.8 | 17.4 | 16.4 | 16.4 | 22-24 | 27-32 | ~ 30 | ~ 21 |
| Screened yield % | 61-63 | | 55.5 | 56.1 | 54.4 | 48-53 | 51-53 | ~ 60 | 38-46 |
| SR number | | 42 | 25 | 25 | 25 | | | | |
| Tensile index N.m/g | | 86 | | | | | | | 50 |
| Burst index kPa.$m^2$/g | | 4.3 | 2.43 | 3.24 | 2.99 | | | 4.4 | |
| Tear index mN.$m^2$/g | | 4.4 | 5.9 | 7.3 | 6.1 | | | 9.9 | 7.8 |
| Brightness % ISO | 49-62 | | | | | | | | |
| Reference | *(36)* | *(37)* | *(38)* | *(38)* | *(38)* | *(39)* | *(39)* | *(39)* | *(40)* |

viscosity, brightness and the strength properties of AS-AQ pulps are superior to those of soda and soda-AQ pulps (*18*).

The potassium based alkaline sulphite method was also developed for agricultural residues (*32*). The process arose from studies of biomass potassium management involving the pulping of agricultural fibrous raw material. The chemical recovery systems used in sodium-based wood pulp mills are problematical for use in agri-pulp mills. Wong has suggested that alternatives to manage the biomass potassium are to provide continual discharge of effluent in the form of usable fertilizer by implementing ammonium-based or potassium-based pulping (*33*). However, ammonium-base pulp has low brightness which would require more extensive bleaching. Potassium based process shows equivalent pulping rates and produces pulps of similar quality to sodium pulping in straw pulping tests (*34*).

## ORGANOSOLV METHODS

Organosolv cooking methods (solvent based) are based on cooking with organic solvent such as alcohols or organic acids. Solvents are used alone or in combination with other chemicals. Methanol and ethanol are common alcohols used, as are formic acid and acetic acid. Other more exotic solvents include various phenols, amines, glycols, nitrobenzene, dioxane, dimethylsulfoxide, sulfolane, and liquid carbon dioxide (*35*).

Various methods have been developed but many of them have not progressed past the laboratory test stages. Organosolv methods based on alcohols or organic acids have been tested at pilot scale but none of these processes is in full mill scale production yet.

If organic solvents are used in an alkaline process, the process requires both alkali recovery and solvent recovery systems, which complicates the recovery system.

This section discusses the methods that use either alcohols or organic acids as cooking chemicals. High cooking temperature and thus high pressures are needed when alcohols are used in cooking. However, organic acids require lower temperatures and the pressure is close to atmospheric. Table 7 presents a selection from the literature of pulping options and resultant pulp properties of organosolv cooking methods using alcohols and Table 8 presents similar information for methods using organic acids.

### Pulping with methanol

Methanol has been used in kraft, sulphite and soda pulping. Demonstration plants using the alkaline sulphite-anthraquinone-methanol process (ASAM) and the soda pulping method with methanol (Organocell) have been built. (The ASAM method is also considered as a modified sulphite cooking method in many quarters.) The use of methanol may be hazardous however, since methanol is a highly flammable and toxic chemical.

The active cooking chemicals of the ASAM process are sodium hydroxide, sodium carbonate, and sodium sulphite. The addition of methanol to the alkaline sulphite cooking liquor improves delignification considerably and the process produces pulp with better strength properties, higher yield and better bleachability compared to the kraft process (*41*) (*18*). The cooking liquor contains about 10% methanol by volume and 0.05 - 0.1% by weight on wood of anthraquinone. The cooking temperature is 175°C and the cooking time is 60-150 min. The higher temperature and the use of methanol mean that the maximum pressure exceeds 10 bars. By varying the ratio of sulphite to sodium bases, the hemicellulose content can be controlled and therefore also the yield and optical properties of the pulp (*42*).

A new process, the FreeFiber process, is under development by Metso (*43*). The process includes sodium carbonate impregnation prior to cooking in gaseous methanol. After the impregnation the excess liquor is removed and concentrated for reuse and the raw material is brought in contact with a gaseous methanol in the heat-up stage. Condensation of the heated methanol releases energy, thus heating the chips to the reaction temperature. The temperature is maintained by adding methanol as required. After the reaction period the pulp is washed and cooled The process does not present obvious economic advantages at the moment but the pulp properties are claimed to be attractive for further investigation (*37*).

The Organocell process uses only methanol, sodium hydroxide and catalytic amounts of anthraquinone as cooking chemicals. Originally the Organocell process was a two-stage process in which the first stage was a mildly acidic stage and the second stage was an alkaline stage. In the first stage cooking was performed with aqueous methanol at 190-195°C. The second stage was carried out in aqueous methanol-sodium hydroxide solution at temperatures up to 180°C. The process has been tested at 5 tpd demonstration plant level. Fluctuations in temperature at such high temperatures cause significant variation in the blow line kappa number. However, it has been shown that the first stage can be eliminated from the process. The cooking temperature of such a one-stage Organocell process can be lowered to 170°C, where the methanol content of the cooking liquor is 30% by volume. The one-stage process is therefore easier to control and the elimination of the first stage results in stronger fibres than those from the two stage process (*44*).

## Pulping with ethanol

The alkaline sulphite-anthraquinone-ethanol (ASAE) process is a modification of the ASAM process. Due to the higher boiling point of ethanol, cooking under lower pressure is then possible. However, the quantity of ethanol required is larger than the amount of methanol needed in ASAM cooking. Wheat straw ASAE pulps have lower lignin content, better physical properties, higher yield and can be easily beaten, resulting in savings in papermaking energy consumption compared to kraft pulps (38).

The ALCELL process uses an aqueous solution of ethanol as the sole delignifying agent. The process has been tested in a demonstration plant which can produce 15 tonnes of unbleached pulp per day. The cooking medium in the ALCELL process is a 50% (weight/weight) ethanol/water mixture. Cooking temperature is in the region of 195°C. Nitrogen is used to maintain a slight overpressure in the cooking vessel. No acid or alkali is added to the cooking liquor and therefore the pH is about 4 due to deacetylation of raw-materials (*45*). The ethanol is recovered by distillation. Lignin and furfural, acetic acid and hemicellulose sugars are the major by-products from the wheat straw ALCELL process. The major part of the silica remains in the pulp, 13-15% of the raw material silica enters the cooking liquor, around 5% leaves the alcohol recovery system with the lignin and the remaining 8% can be removed with the xylose rich stillage steam (*39*).

The IDE process is a sulphur free alkaline pulping process, where ethanol and anthraquinone (AQ) are used to significantly speed up delignification (*40*). The IDE process includes three consecutive steps: impregnation (I), depolymerisation (D) and extraction (E). In the first step, the raw material is subjected to a strong aqueous sodium carbonate solution. In the second step, the raw material is cooked in an aqueous ethanol solution to achieve bulk delignification. In the third step, the degraded lignin is extracted from the pulp with a fresh ethanol-water solution. An IDE pulp mill can be economically feasible on a small scale and can be located close to fibre resources (*46*). The silica in the raw material is extracted into the impregnation liquor from where it is easier to remove than from the black liquor. In trials with wheat straw, yields of over 50% were achieved, with residual lignin below 2.5% (*47*).

The Punec process is a pulping method that uses ethanol, anthraquinone and caustic soda as cooking chemicals. The raw material is firstly treated with aqueous alcohol after which delignification is performed in a high pressure digester. The lignin and hemicellulose are dissolved into the cooking liquor and flashed into a flash tank after which lignin is separated from the flash liquor by acidification. The hemicellulose rich liquid is then distilled to recover the remaining alcohol. Finally the aqueous fraction of hemicelluloses is treated anaerobically to produce biogas, or converted into animal feed, or fertilizer. The process has been tested in a 4 tpd demonstration plant but no information on the exact process conditions or the pulp quality is available. The process is claimed to be pollution free (*48*) making the process worthy of more investigation.

## Pulping with organic acids

Typical organic acids used in acid pulping methods are formic acid ($K_a=1.8*10^{-4}$) and acetic acid ($K_a=1.7*10^{-5}$). Formic acid can also be used to enhance acetic acid pulping. The temperature and pressure can be lower when formic acid is used in pulping compared to that used in alcohol or acetic acid pulping (*49*). Acetic and formic acid react with lignocelluloses during delignification forming corresponding esters (*50*). Formic acid and acetic acid are also formed during the acidic processing of lignocelluloses and this is an advantage of the processes using formic and acetic acid (*49*). However, organic acids, especially formic acid, are highly corrosive and cause severe corrosion problems in process equipment.

The Milox process is an Organosolv type process. The cooking chemical used is peroxyformic acid or peroxyacetic acid, which is produced in-situ from hydrogen peroxide and formic or acetic acids. The hydrogen peroxide consumption is reduced by performing the process in two or three stages. In the three-stage Milox process, acetic acid or formic acid is refluxed with the pulp in an intermediate stage without peroxide. The two-stage peroxyacetic acid process gives higher delignification than the three-stage process and vice-versa with peroxyformic acid (*54*).

The Milox process is a sulphur free process and bleaching can be achieved totally without chlorine chemicals. Recovery of cooking chemicals from the Milox process has caused problems. Some acetic acid is formed as well as formic acid, and the separation of the acetic acid, formic acid, water mixture is best achieved by extractive distillation. Butyric acid is suggested as a solvent for the distillation. The Milox process would be more economical to operate if a mixture of acetic acid and formic acid could

**Table 8**
**Pulping conditions and pulp properties of organic acid cooking**

| Process<br>Raw material | Chempolis<br>Wheat straw | CIMV<br>Wheat straw | CIMV<br>Bagasse | CIMV<br>Rice straw | CIMV<br>Rice straw |
|---|---|---|---|---|---|
| Formic acid % | | 60 | 30 | 30 | 20 |
| Acetic acid % | | 20 | 55 | 50 | 60 |
| Water % | | 20 | 15 | 10 | 20 |
| Temperature °C | | 107 | 107 | 107 | 107 |
| Time min | | 120 | 180 | 120 | 180 |
| Kappa number | 6.1 | 50.4 | 28.2 | 34.6 | 45.8 |
| Yield % | | 43 | 49.4 | 47.5 | 52.9 |
| SR number | 42 | 49 | 45 | | 45 |
| Tensile index N.m/g | 53 | | | | |
| Burst index kPa.m$^2$/g | 2.4 | 2.14 | 3.21 | | 2.52 |
| Tear index mN.m$^2$/g | 2.35 | 3.27 | 4.23 | | 4.38 |
| Brightness % ISO | | 36.5 | | | |
| Reference | (*37*) | (*51*) | (*52*) | (*53*) | (*53*) |

be used as solvent and this is a technical possibility (*55*).

The Chempolis pulping process is based on cooking with formic acid. The process is a one-stage approach, cooking temperature is 110-125°C and cooking time is 20-40 min. In addition to formic acid, acetic acid can also be used in the process, a small amount of which is formed during the process. After cooking, the pulp is washed and pressed in several stages (between 2 and 6) with formic acid. The last washing stage is at high pulp consistency with performic acid. The acid is then removed from the pulp by washing with water. Lignin, hemicelluloses and fatty acids are washed from the pulp in an acid washing stage. Finally the unbleached pulp is bleached with alkaline peroxide (charge 3-6.5% $H_2O_2$) (*56*). Formic acid and acetic acid percentages have ranged from 80/15 to 40/40 respectively (the balance being water) (*57*). Reported bleached pulp yield is 39% (*37*). Spent cooking liquor can be evaporated to 90% dry solids without viscosity problems because silica does not dissolve in the cooking liquor. After evaporation the spent liquor can be incinerated. Evaporation is accompanied by the formation of formic acid, acetic acid and furfural. The formation of formic acid is claimed to reduce the demand for make-up formic acid. As with formic acid, acetic acid and furfural are volatile compounds so they can be separated from evaporation condensates by distillation (*58*).

The Acetosolv process is a hydrochloric acid catalysed (0.1%-0.2%) acetic acid process. The cooking temperature is 110°C, and the process is unpressurised. Dissolved lignin and furfural are by-products that can be obtained from the waste liquors (*59*).

The Acetocell process has been developed from the Acetosolv concept. The pulping is performed with the aid of acetic acid at high temperature without added catalysts. The delignification leads to low kappa numbers at high yields (*60*).

The Formacell process was developed from the Acetocell process. It is an organosolv pulping approach in which a mixture of formic and acetic acid is used as the cooking chemical, acetic acid is 75% and formic acid 10%, the rest being water. The cooking temperature is 160-180°C, after which cooked pulp is washed with acid and bleached with ozone. Dissolving and paper grade pulps can be produced by the Formacell process (*50*).

The CIMV process seems to be a further development of the Formacell approach. A small scale French agro-fibre mill, producing 50000 t of paper and 50000 t of by-products per year, has been announced to be built (2008-2009) in the Champagne-Ardenne area. The CIMV process uses cereal straw or sugar cane bagasse to produce bleached paper pulp, xylose syrup, and sulphur free lignin. Organic acids are recycled from waste liquor via evaporation. Water is used to treat the remaining syrup to precipitate lignins, which are easily separated (*61*). References to this process do not describe the process in detail but it is probably based on the use of acetic acid, formic acid and water as cooking chemicals (formic acid 20-30%, acetic acid 50-60% and 20% water). The process is atmospheric and cooking temperature is close to 100°C (*51,52,62-65*). Pulp bleaching requires 4% peroxide and 12% sodium hydroxide using a PPP peroxide bleaching sequence. Bleached pulp yield is only 32% (*62*).

## CHEMI-MECHANICAL AND OTHER PULPING METHODS

Chemical pre-treatment during the mechanical pulping of wood is known to improve pulp quality and reduce energy consumption and so chemi-mechanical processes for non-wood materials are also of great interest.

Sulphite, sodium hydroxide or alkaline peroxide have been used as pre-treatment chemicals and modifications of the mechanical defibration for non-wood pulps have also been developed, for instance extrusion pulping and steam explosion pulping. It has been shown that biological treatment before chemical treatment (Biopulping) can reduce refining energy consumption, as well as chemical consumption during pulping and negative impacts on the environment (*66*). The advantages of a chemi-mechanical process approach are that the pulp yield is high, chemical recovery is not necessary and effluents can be treated in biological treatment systems. A selection of the data from the literature, including chemical pre-treatment conditions and pulp properties of chemi-mechanical processes is presented in Table 9.

### CMP and CTMP processes

Chemi-mechanical pulp (CMP) can be produced by refining at atmospheric pressure, however the chemical treatment stage is more severe than in the chemi-thermomechanical (CTMP) process which uses pressurized refining and where relatively low chemical doses are applied (*72*).

CMP and CTMP pulping are carried out at temperatures ranging between 100-160°C for 10-30 min (*73*). The chemical treatment is responsible for fibre softening and decreases the subsequent refining energy requirements. The chemicals used in pre-treatment are sodium sulphite and sodium hydroxide. The sodium sulphite charged and the maximum temperature of pre-treatment influence the degree of sulphonation, and subsequent lignin swelling. The NaOH charge and pre-treatment time have an effect on brightness and pulp yield. Increasing the NaOH charge from 1% to 4% can increase the degree of sulphonation but at the same

**Table 9**
**Pre-treatment conditions and pulp properties of chemi-mechanical pulping methods**

| Process<br>Raw material | Extrusion pulping<br>Wheat straw | Steam explosion<br>Bagasse | APMP<br>Wheat straw | APMP<br>Kenaf | APMP<br>Kenaf | APMP<br>Bagasse |
|---|---|---|---|---|---|---|
| $Na_2SO_3$ charge % as NaOH | - | 8 | - | - | - | - |
| NaOH charge % | 3 | 1 | 3 | 3 | 3 | 10 |
| $H_2O_2$ charge % | - | - | 3 | 3 | 2 | 3 |
| Temperature °C | 140 | 190-210 | | 90 | 80 | |
| Reaction time min | 120 | 1-4 | | 50 | 40 | |
| Screened yield % | | 60 | 84 | | | 71 |
| SR number | 35 | | | 56 | 61 | 20 |
| Tensile index N.m/g | | 56 | | | | |
| Burst index kPa.$m^2$/g | 2.41 | 3.00 | | | | 2.38 |
| Tear index mN.$m^2$/g | 3.2 | 5.7 | | 4.2 | 3.7 | 3.0 |
| Brightness % | | | 50.0 | 53.2 | 54.0 | 72.1 |
| Reference | (*67*) | (*68*) | (*69*) | (*70*) | (*70*) | (*71*) |

time the brightness and the yield (of unbleached giant reed pulp) decreases. High pre-treatment temperature decreases pulp yield, with the optimum temperature being 140°C (*74*).

### APMP method

The APMP process is based on the incorporation of peroxide bleaching in the chemical impregnation and refining stages in which bleaching action is used to not only to eliminate alkali darkening but to brighten the pulp as well. The chemicals used in APMP are sodium hydroxide and hydrogen peroxide. Inhibitors such as diethylenetriaminepentaacetic acid (DTPA), magnesium or silicate must be used to reduce the degradation of peroxide (*75,76*).

A typical APMP process consists of two impregnation steps, a first stage performed with a chelating agent, residual caustic and peroxide and after that the raw material is steamed. The second stage is impregnation with alkali, peroxide and more chelation agents to remove metal contaminants. The process is performed at high consistency 20-45% (*76,77*). The temperature range reported during impregnation is from 85°C (*78*) to 95°C (*71*). Chemical charges depend on the non-wood raw material used. Kenaf APMP requires 4.0% NaOH and 3.1% $H_2O_2$. The charges are much higher for straw (*78*) and bagasse (*71*).

### Steam explosion pulping

The steam explosion pulping (SEP) process consists of the chemical impregnation of raw material, saturated steam cooking for short periods, rapid pressure release, atmospheric refining and, if necessary, bleaching. The impregnation solution is 8% sodium sulphite with, optionally, 1% sodium hydroxide, magnesium chloride, sodium bicarbonate or magnesium carbonate. With SEP it is possible to produce high brightness pulps at about 90% yield (*79*).

The cooking stage in SEP is short (< 5 min), carried out at high temperature (180-210°C) (*80*). The presence of swelling agents (NaOH, $NaHCO_3$, $MgCO_3$) in the impregnation solution leads to a decrease in the required refining energy (*73*).

The SEP method is well suited for non-wood pulping. The pulp properties of steam explosion are equal to or better than the properties of CMP and CTMP pulps (*81*). The yield of SEP pulp is, however, lower than that of CMP and CTMP (*73*).

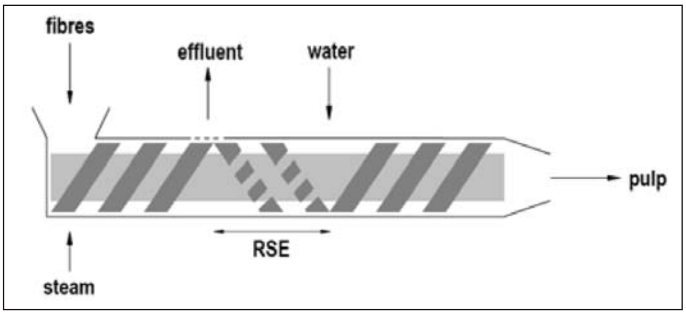

**Fig. 1 Side view diagram of the pulping extruder (*83*)**

### Extrusion pulping (Bivis)

Extrusion pulping is carried out mechanically or chemi-mechanically, using compression and shear forces to process the fibres (*82*). Extrusion pulping is based on the use of internal co-rotating intermeshing screws in the process vessel. Fibrous raw material is fed into the barrel by transport screws. The main screw element used in the extrusion pulping processes is the reversed screw element (RSE). The RSE is a threaded element with opposite pitch to that of the transport screws. This results in accumulation and compression of fibres in the space between the transport screws and the RSE (83). A side view of the pulping extruder is presented in Figure 1.

The high compression and shear forces generated cause defibration, fibrillation and the shortening of fibres. Excess filtrate is pressed out through barrel filters and placed upstream from the RSE. The pressure drop created in passing the RSE heats the pulp and provides rapid impregnation of liquids which can be supplied through an injection port down-stream from the RSE. This combination of transport screw, RSE, filter and injection port can be repeated along the barrel (83).

The chemical charge in the extrusion pulping of wheat straw is 3%, temperature 140°C and pressure is 6-7 bar. Pulp is further reacted in a retention chest for 120 min at 100°C (*67*). The energy consumption of extrusion pulping is lower than that of the CMP process (*84*).

Non-wood pulp is being produced by extrusion pulping at full mill scale. The Bivis process is claimed to require less chemical addition, water, power, space and manpower than alternative systems. High yields are also promised (*85*).

### Mild acid cooking method

In an effort to further simplify the non-wood pulping process, a process involving cooking under mildly acidic conditions has been proposed (*86*). The idea of the process is to utilize the unique structure of annual plants in terms of their low lignin content. Processing is via a low temperature, un-pressurized, mildly acidic stage where the raw material is essentially cleaned/cooked using a liquor containing a mixture of formic and acetic acids, and chelating agents. The actual defibration then takes place in subsequent peroxide bleaching stages. Although capable of small scale operation without recovery, the effluents from the mild acid cook and bleaching stages can be easily treated for instance in traditional biological effluent treatment systems. The process is simple and does not require special process equipment. In the case of wheat straw, a pulp with an ISO brightness of over 80% and a yield of over 50% is achievable (*86*). Silica is partly extracted into the bleaching effluents.

## CONCLUSIONS

With annual plant materials, neutral and alkaline sulphite pulps are generally comparable, but have higher yield and brightness than alkaline pulps.

Processes that use both alkali and alcohol need recovery systems for both chemicals, which raise the investment cost.

High cooking temperature and thus high pressure is needed when alcohols are used. The use of organic acids as cooking chemicals is possible at lower temperatures and close to atmospheric pressures but these pulps need large quantities of bleaching chemicals. The bleached pulp yield is also low and the pulp properties poor. An advantage of organosolv processes is the formation of useful by-products such as furfural, lignin and hemicelluloses.

The pulp yield in chemi-mechanical processes is high and the chemical charges low, hence chemical recovery is not necessary. Pulp quality is moderate, but the process requires refining energy.

None of the above processes seem to fully exploit the particularities of the non-wood raw materials as compared to wood. The mild acid cooking offers an interesting avenue in the search for non wood pulping alternatives with potential to address the need for economically competitive small scale pulping processes for non-wood materials.

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Paper II

# Producing pulp and energy from wheat straw

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# Producing pulp and energy from wheat straw

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## SUMMARY

The aim of this study was to evaluate the use of wheat straw as a raw material in simple biorefinery operations producing papermaking pulps and energy. The first option was to produce pulp for printing and writing papers by hot water treatment followed by alkaline peroxide bleaching. The second option was to produce unbleached pulp for packaging materials by a hot water treatment method, followed by mechanical refining. In both options residual materials are available for energy production, in the form of fines or dissolved solids.

The results from the chemical approach showed that the optimum hot water treatment temperature is close to 100°C and acid is not needed in the stage. Less than 10% of wheat straw is dissolved in these hot water treatment conditions with a temperature below 130°C. Following alkaline bleaching it is possible to produce pulp with over ISO 75% brightness and a yield of over 50%. Paper properties of the resultant wheat straw pulp are relatively good. The results of the mechanical approach showed that 36% of the original wheat straw ends up in the fibre fraction between 30-100 mesh, 13% is coarse fines between 100-200 mesh and 41% of the original raw material is fine fines below 200 mesh.

The papermaking properties of the fibre fraction thus obtained were relatively poor suggesting that they could only be used in mixtures with other pulps, or as such in moulded fibre packages.

**KEYWORDS**

Non-wood fibre, wheat straw, biorefinery, hot water treatment, bleachability, pulp properties, mechanical refining, fines

## INTRODUCTION

Despite the growing interest in biomass, annual biomass is still poorly exploited (*1-3*). High value-added products such as papermaking fibres or packaging materials could potentially be produced from field grown biomass, but there are significant well known problems related to non-wood fibre usage. For example, the often quoted silica problems (*4*) related to annual plants need to be overcome.

In considering biorefineries, one concept is that annual plant fibres, as a papermaking raw material, could be part of a complete utilisation chain, where the most valuable fraction is used for human or animal food or commodity production; suitable fractions of the plant are utilised in producing raw material for papermaking, while the low value fraction and dissolved sugars are utilised directly for energy production.

In fact modern kraft pulp mills can already be considered to be first generation biorefineries (*5*), where wood is exploited for both fibre and energy production with about half of the incoming wood being dissolved in the cooking liquor. The resulting black liquor is evaporated and incinerated to release energy that is used to generate steam and electricity exceeding internal mill energy needs; hence modern kraft mills produce excess energy from their own waste (*6*).

But the kraft process is a multi-stage process with high investment costs and thus pulp mills are economically competitive only if mill sizes are large enough to benefit from economies of scale. Issues related to the local availability of non-wood raw materials reduce the potential size of any pulp mill based on non-wood material so, even if operating difficulties can be overcome, the resulting kraft non-wood pulp mills would be less cost-effective (*7*).

In an effort to simplify the non-wood pulping process, a process involving treatment under mildly acidic conditions has been previously proposed (*8*). Processing is conducted via a low temperature, unpressurised, mildly acidic stage where the raw material is essentially cleaned/treated using a liquor containing a mixture of formic and acetic acids, and chelating agents. The actual defibration then takes place in subsequent peroxide bleaching stages. The effluents from the process can then be easily treated, for instance in traditional biological effluent treatment systems.

In this study, extensions of this basic concept have been studied in a search for a novel biorefinery exploiting field grown biomass for local, flexible, fibre and energy production. The study includes two approaches based on an initial hot water treatment: the “chemical” in which peroxide bleaching is then used to produce pulp for printing and writing papers and the “mechanical” in which the unbleached material from the first stage is mechanically refined to produce fibres for packaging grade papers. In both approaches the idea is that the residue is then used for energy production. The biomass studied is wheat straw and the study also seeks to further investigate best conditions for the initial hot water treatment.

## PROCESS SCHEMES

The first process studied was to treat wheat straw raw material with hot water and then by a P-P-Paa-P bleaching sequence, (alkaline peroxide (P) and peracetic acid (Paa)). The resultant fibre fraction is then scheduled for paper making and the dissolved sugars from the hot water treatment and bleaching stages, used for energy or chemicals production. The final effluents could be treated in traditional waste water treatment systems.

The second option studied aimed to minimise the use of chemicals in the process. Because wheat straw does not defibrate during hot water treatment alone some mechanical energy is needed and this is achieved through traditional papermaking refiners. The idea behind this scheme is thus to produce unbleached fibres that might be suitable for packaging

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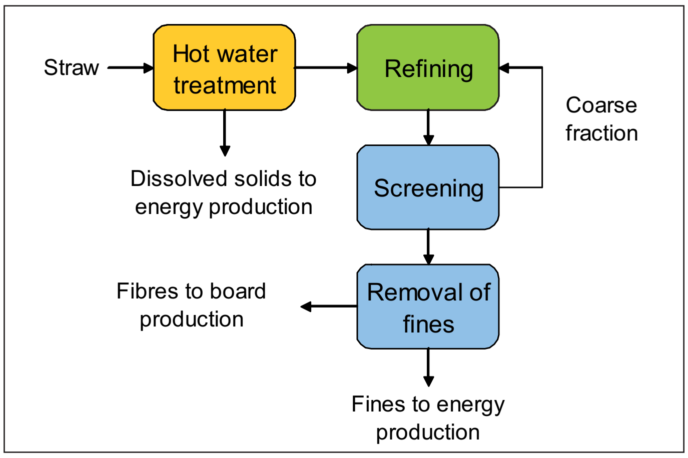

**Fig. 1 The low-chemical process scheme**

papers and to utilise the remaining material in the form of fines or dissolved solids for energy production. The process concept is described in Figure 1.

The easily dissolved solids are separated by hot water treatment and then the treated straw is mechanically refined and fractionated. The fibre fraction is used in board production, the coarse fraction is returned to refining and fines, which hamper drainability, are removed and used in energy production.

Both these process schemes have specific advantages. Note that in the chemical option, only oxygen based chemicals are required for bleaching. In the mechanical option the fines, which cause poor drainage and low papermaking production rates, are removed and utilised profitably in energy or fuel production. Note also that ethanol or biogas can be produced with known methods from fines and dissolved solids.

Either of these two process options could possibly be integrated with an existing pulp or paper mill, or a de-inking plant using recycled papers. Both concepts can be considered as second generation biorefinery concept, concepts producing fibres, energy and fuels for sale.

## EXPERIMENTAL

### Raw material

The spring wheat straw species used in the hot water treatment optimisation experiments was the Finnish Kruunu variety and it was cultivated in Jokioinen, Finland, during summer 2006. The straw was harvested and cut into 5 cm sections with a bale chopper and dried to about 90% dry content.

The spring wheat straw species used in the mechanical refining experiments was Marble variety and it was cultivated in Jokioinen, Finland in summer 2007. The straw was harvested and cut into 5 cm pieces with a harvester chopper and dried to about 90% dry content.

The straws were screened with laboratory screens described in standard SCAN-CM 40:88 to remove fine particles. The screening time was 30 s and pieces above 6 mm were accepted for the experiments.

### Hot water treatment

The hot water optimisation study was carried out over the temperature range 70-150°C. For temperatures above 100°C the treatment was carried out in an air-heated digester equipped with six 2.5 L autoclaves. Treatments below 100°C were carried out in polyethylene bags in a water bath. Samples of 75 g (bone dry) straw were used. The time at treatment temperature was 60 min except that a 150 min treatment time was also tested for selected test points. Water to straw ratio was 10:1 The acid charge in hot water treatment was 0-2.3% on the straw. The acid was a mixture of formic (25%) and acetic acid (75%). DTPA (charge 0.2% on straw) was used as a chelating agent in the treatments.

The straw for mechanical refining experiments was treated in a rotating 16 L Teflon coated digester. Hot water treatment temperature was fixed at 120°C and time at treatment temperature 60 min. The water to straw ratio was 10:1. No chemicals were added during this hot water treatment.

After hot water treatment, the straw was washed. Washing was carried out by diluting the treated straw with deionised water, agitating, allowing to settle for 2 minutes and removing the excess water through a wire pouch. Dilution and thickening was repeated 3 times. Finally, the treated straw was centrifuged to 25% consistency.

### Bleaching

Bleaching after hot water treatments was carried out in polyethylene bags in a water bath. The chemical charges were calculated on the initial amount of straw. The pulps from three separate bleachings after hot water treatment without acid addition were mixed carefully after every stage and then divided into three portions for the next bleaching stage. The bleaching conditions are presented in Table 1.

After each bleaching stage the pulp was washed by the dilution and thickening method as explained above. After the last bleaching stage and wash, the pulp was acidified. The pulp was diluted with deionised water and dilute sulphuric acid was added, until the pH reached roughly 3.8. After 15 minutes, the final pH was between 4 and 4.5. After acidification the pulp was washed again as explained before.

### Reference soda cooking

Reference soda cooking was performed in the 2.5 L autoclave of the air heated serial digester. The cooking temperature was 160°C, time at cooking temperature 60 min, NaOH charge 14% and liquor to straw ratio 5:1.

### Mechanical refining

The hot water treated straw was preheated in the feeder of the batch type VTT wing

**Table 1.**
**The bleaching conditions of hot water treated straw. P-P-Paa-P bleaching. P alkaline peroxide stage, Paa peracetic acid stage.**

| | |
|---|---|
| **P1 stage** | |
| Temperature, °C | 85 |
| Time, min | 180 |
| Consistency, % | 10 |
| NaOH charge, % on straw | 7.0 |
| $H_2O_2$ charge, % on straw | 4.0 |
| **P2 stage** | |
| Temperature °C | 85 |
| Time, min | 180 |
| Consistency, % | 10 |
| NaOH charge, % on straw | 1.0 |
| $H_2O_2$ charge, % on straw | 2.0 |
| **Paa stage** | |
| Temperature, °C | 85 |
| Time, min | 60 |
| Consistency, % | 10 |
| NaOH charge, % on straw | 0.2 |
| Paa charge, % on straw | 1.0 |
| | **P3 stage** |
| Temperature, °C | 85 |
| Time, min | 180 |
| Consistency, % | 10 |
| NaOH charge, % on straw | 1.0 |
| H2O2 charge, % on straw | 2.0 |

**Fig. 2 VTT Wing refiner used in the refining experiments.**

refiner (Fig. 2) for 300 s before feeding with a piston to the refiner. The amount of straw in refining was 75 g, the feeding time 12 s and the initial temperature of the feeder and the refiner 120ºC. The speed of rotation was 1500 r/min and the distance between stator and rotor 0.5 mm. The pressure during refining was 2.5 bars and it was controlled by a pressure relief valve. Additional water 120-140 g/min was fed into the refiner to control consistency during refining. The variable in refining was refining time 30-120 s.

The coarse fraction was separated from selected pulps by screening with a Valmet TAP03 laboratory screen with the slot size of 0.13 mm. The coarse fraction was refined again at the same conditions as the refining of straw, excluding the amount of coarse fraction which was 50 g and the refining time 120-150 s.

### Chemical analyses

The gravimetric lignin content of the wheat straw was measured according to the method of Browning (*9*). The monosaccharides were determined after acid hydrolysis treatment with HPAEC analysis (Dionex ICS-3000 liquid chromatography) according to the method of Hausalo (*10*). The extractives were analysed according to modified SCAN-CM 49:93 test method. Before measuring the ash content of the straw, the sample was ground and dried at 105°C temperature. The ashing was conducted at 550°C for 12 hours.

### Bleached pulp and soda pulp analyses

Before preparing handsheets the bleached pulp was wet disintegrated according to the test method ISO 5263 and screened on a Mänttä flat screen using a screen plate with a slot of 0.25 mm. Laboratory hand sheets and paper technical properties were measured according to SCAN and ISO test methods. Kappa number of the soda pulp was determined according to the ISO 302/2004 method.

### Mechanical pulp analyses

The mechanically refined pulp after hot water treatment was fractionated with a Bauer McNett apparatus according to standard SCAN-M 6:69. The plates used were 16, 30, 100 and 200 mesh. The fibre length of the fibre fraction between 30-100 mesh was measured with FiberMaster apparatus. Photographs under microscopy of the fractions were also taken.

100 and 200 mesh fractions were combined and the paper technical properties were analysed according to SCAN test methods. In addition, the properties of the wheat straw pulp when reinforced with softwood pulp were analysed. The softwood pulp was beaten with a Valley Hollander according to the SCAN test method. The proportions of wheat straw pulp were 0, 20, 40, 60, 80% with 10 minutes Valley beaten softwood mill pulp.

### Chemical treatments of refined straw

The alkaline peroxide treatment of refined straw 100 and 200 mesh fractions was performed in a polyethylene bag in a water bath. The conditions were 85°C, 3 h, 5% NaOH, 4% $H_2O_2$, 0.25% MgSO4 and 0.2% DTPA.

The dry wheat straw/softwood mix handsheets were treated with 1.0 g/L cationic starch solution with a device constructed by VTT, Jyväskylä. The starch used was Raisamyl 135 and the amount was 1% or 2% of total dry weight onto the fibre network.

Basically the surface applications were applied as follows. A single laboratory handsheet (area 14.1 cm X 14.1 cm) was passed at constant speed below a spray head. The starch spray was automatically controlled to start and stop spraying as and when the sheet was below the spray. The sheet was dried on a laboratory cylinder drier after each single-pass spray application. The surface temperature of the cylinder dryer was 100°C and the drying time 45 s for each sheet. The sheets were treated to either a single-sided or double-sided spray-application. The sprayed volume was determined by weighing the sheet both before and after the spraying. Each single pass applied 0.8 mL of solution to the sheet. Taking into account volume and consistency of sprayed starch, each single-pass spray application introduced 1% starch of total dry weight.

## RESULTS AND DISCUSSION

### Chemical composition of wheat straw

The straw screening removed 38.9% of the original cut wheat straw raw material as fine particles. The fines fraction also contained < 2-3 cm particles from the stem. The screening was, however, needed to ensure that the straw could be thoroughly mixed and equally distributed in portions before processing it, because the fines tend to separate from the straw and hence cause an uneven distribution in batches. The straw fines contain somewhat more ash (Table 2), and notably more silica. Silica is distributed throughout the straw stem, but it is concentrated in the leaves and outer surface of the stem. Straw cutting may cause higher concentrations of the silica in the fines part and the screening can also separate part of the silica from the outer layers of the straw causing this higher silica content in the fines fraction.

Table 2 also presents the chemical composition of the wheat straw used in the hot water treatment optimisation experiments and the chemical composition of the hot water treated straws.

The lignin content is close to the upper limit and the hemicelluloses content close to the lower limit of the reported ranges for wheat straw, 16-21% and 26-32%, respectively (*11*). The ash content is within the range reported for wheat straw, 4-9% (*11*). The straw contains quite a lot of silica and magnesium, which are usually used as stabilisers in alkaline peroxide bleaching. The yield of the hot water treatment is high due to the mild conditions in treatment (Fig 6). The chemical composition, especially the lignin content, does not significantly change during treatment. About 1/3 of the yield loss comes from the reduction of ash content. Some water soluble carbohydrates are also dissolved during hot water treatment.

## Need of chelating agents in peroxide bleaching

In conventional peroxide bleaching the excessive decomposition of peroxide is usually controlled by removing the harmful transition metals from pulp just before an alkaline peroxide stage. Acid washing and chelation are the practical means to achieve good control. Magnesium salts and/or silicates can be used as stabilisers. The most frequently applied technique is to use chelation at pH 4-7 and to wash out the chelated metals at a later stage in a washer. Further improvements are achieved by using a magnesium salt as a protective additive in the peroxide stage. The control of the molar ratios of magnesium and manganese in peroxide stages is essential for effective magnesium use. A Mg/Mn molar ratio of over 30 is appropriate at 90°C (*12*).

It appears that the hot water treatment may act as a chelation/cleaning stage. This can be seen in the clear reduction of the harmful metals: manganese, iron and copper (Table 2). The need for extra stabilisers in peroxide bleaching was studied by adding magnesium, DTPA and/or sodium silicate to the first alkaline peroxide stage. The response was measured as brightness after the bleaching.

The finding was that the best final brightness was achieved when no stabilisers – sodium silicate, DTPA or $MgSO_4$ was added to the peroxide stage. This may be explained partly by the previous hot water treatment and its chelation effect but partly also by the naturally high silica and magnesium content of wheat straw. The in situ Mg/Mn molar ratio of the natural untreated wheat straw and also the ratio of hot water treated wheat straw materials are much higher than the appropriate level needed. Pan and Leary (*13*) and Eroglu (*14*) have also reported that the addition of stabilisers was not necessary in wheat straw bleaching or oxygen delignification. However, stabilisers may still be needed in some cases depending on the nature of the raw material used. In this case, it was decided not to use any stabilisers in peroxide bleaching.

## Justification of hot water treatment

The small changes in chemical content with the hot water treatment raises the question of whether the hot water treatment is needed at all. A reference bleaching was therefore performed without a prior hot water treatment. The defibration of the straw was remarkably worse without the prior hot water treatment and the final brightness was as much as 5% units lower compared to the optimum hot water treated and bleached pulp (Table 3). In addition the rejects content of the bleached pulp was 21.6%, approximately three times more than the amount of rejects obtained when the hot water treatment was used. Clearly the hot water treatment is needed before peroxide bleaching for optimal results. In addition to the cleaning effect, the hot water treatment appears to "soften" the wheat straw material before the following bleaching stage.

**Table 2.**
**Chemical composition of wheat straw and hot water treated wheat straw.**

| Sample | Wheat straw (WS) | Wheat straw, removed fines | WS treatment 70°C | WS treatment 95°C | WS treatment 120°C | WS treatment 130°C |
|---|---|---|---|---|---|---|
| **Carbohydrates,** mg/100 mg | | | | | | |
| Glucose | 37.3 | | 38.8 | 39.4 | 39.7 | 39.5 |
| Xylose | 25.6 | | 27.5 | 27.4 | 27.6 | 28.0 |
| Rhamnose | <0.1 | | <0.1 | <0.1 | <0.1 | <0.1 |
| Arabinose | 2.52 | | 2.81 | 2.74 | 2.73 | 2.68 |
| Mannose | <0.1 | | <0.1 | <0.1 | <0.1 | <0.1 |
| Galactose | 0.64 | | 0.66 | 0.64 | 0.64 | 0.59 |
| Monosaccharides, total | 66 | | 70 | 70 | 71 | 71 |
| Polysaccharides (calc) | 59 | | 62 | 63 | 63 | 63 |
| **Lignin, %** | | | | | | |
| Gravimetric lignin | 20.2 | | 20.7 | 20.7 | 20.5 | 19.9 |
| **Acetone extractives, %** | 1.69 | | 1.66 | 1.34 | 1.82 | 1.96 |
| **Ash, %** | 6.8 | 7.9 | 4.9 | 4.7 | 4.4 | 4.2 |
| **Metals,** mg/kg straw | | | | | | |
| Silica | 19900 | 26300 | | | 17800 | |
| Magnesium | 1200 | 1100 | | | 365 | |
| Calcium | 2060 | 2110 | | | 1220 | |
| Kalium | 14000 | 11500 | | | 926 | |
| Iron | 96.3 | 144 | | | 18.2 | |
| Manganese | 11.9 | 14.2 | | | 2.65 | |
| Copper | 3.53 | 3.38 | | | 1.95 | |

## Acid charge in hot water treatment

The effect of acid charge in hot water treatment on the final brightness of bleached wheat straw was studied (Fig. 3). The results indicate that the best brightness values were achieved when no acid was added to the hot water treatment.

To understand why this should be the case it should be noted that in wood based (*15*) and model compound based (*16*) research when the autohydrolysis pH is decreased the lignin structure also alters. Similarly, in slightly acidic conditions (pH 2 - 5) parts of the acid-soluble, low molecular weight lignin is mobilised, parts of it even dissolve in the water and parts remain in the cell wall layer even though their molecular weight is decreased.

Hence, for hot water treatment of wheat straw the lower the pH and the higher the temperature the more lignin is altered, and this is also reflected in the final brightness. The pH after the hot water treatment depends on the treatment temperature and the acid charge added, as expected, see Figure 4.

## Hot water treatment temperature

The temperature range 70-150°C was studied to find the optimum hot water treatment temperature. A temperature of 70°C is typical for a chemical pulp chelation stage and 150°C is a temperature where lignin reactions are known to take place. Figure 5 presents the brightness after every bleaching stage as a function of the hot water treatment temperature. No acid was added during treatment. Figure 6 presents the yield after hot water treatment and after the following bleaching stages as

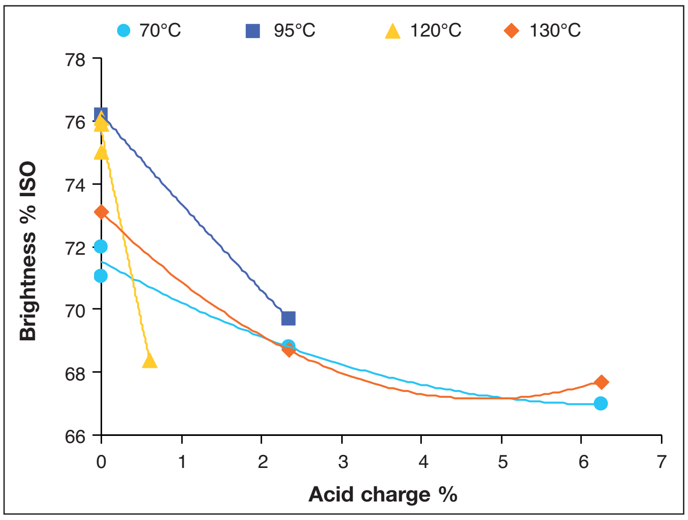

**Fig. 3** **Wheat straw pulp brightness after P-P-Paa-P bleaching as a function of acid charge and hot water treatment temperature. P alkaline peroxide stage, Paa peracetic acid stage.**

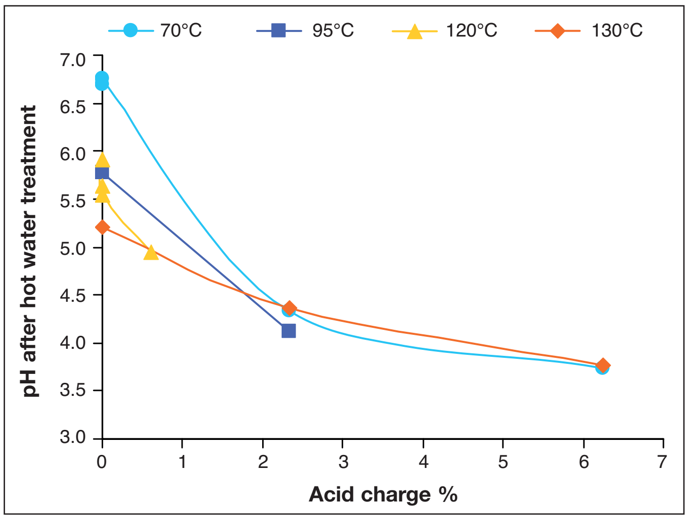

**Fig. 4** **pH after hot water treatment of wheat straw as a function of acid charge and hot water treatment temperature.**

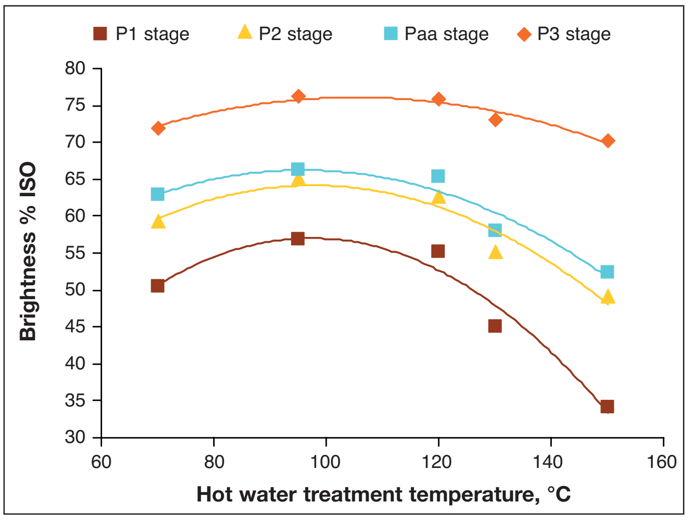

**Fig. 5** **Wheat straw pulp brightness after bleaching stages as a function of hot water treatment temperature. P alkaline peroxide stage, Paa peracetic acid stage.**

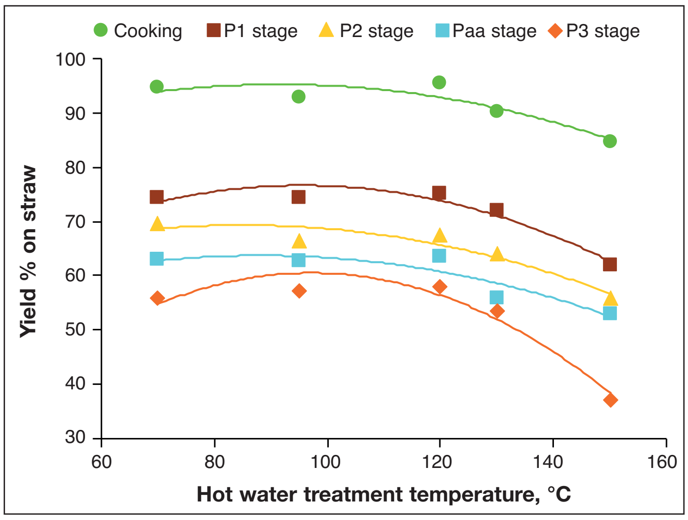

**Fig. 6** **Wheat straw pulp yield after hot water treatment and bleaching stages as a function of hot water treatment temperature. P alkaline peroxide stage, Paa peracetic acid stage.**

a function of the treatment temperature. These results are average values of three separate bleachings as explained in the materials and methods section.

Highest brightness values are achieved near the temperature value 100°C. A temperature of 70°C is too low and an explanation could be that the structure of wheat straw may not loosen enough. A temperature of 130°C is too high and this may be because it induces irreversible reactions of hemicelluloses and lignin that worsen the bleachability. In addition the bleached pulp yield is highest when the hot water treatment temperature is close to 100°C.

## Hot water treatment time

The effect of extending hot water treatment time was studied at selected temperatures. No advantage in the following bleaching step was gained by extending hot water treatment time from 60 to 150 minutes.

## Potential paper properties of bleached wheat straw pulps

The laboratory paper properties of the bleached wheat straw pulps are presented in Table 3. The strength properties are quite good for a wheat straw pulp. The reference wheat straw soda pulp with kappa number 17.7 and screened yield 49.1% from the same raw material gave tensile index 57.7 N.m/g and tear index 5.9 mN.m$^2$/g. The brightness of soda pulp was also notably lower ISO 30.1%, as expected. The drainability is low, as usual with straw pulps. This could be compensated by removing fines, at the same time having a positive effect on paper bulk. The strength properties of the bleached pulp compared to reference bleached pulp without hot water treatment are improved. Further information on the properties of non-wood pulps from alternative, existing pulping processes was presented in an earlier review (*17*).

These studies show that hot water treatment followed by alkaline peroxide bleaching consumes large amounts of sodium hydroxide in bleaching to the target brightness of ISO 75–80%. In practice this means that the process would need some kind of chemical recovery system unless the bleaching chemical consump-

**Table 3.**
**Paper properties of the wheat straw pulp after P-P-Paa-P bleaching as a function of hot water treatment temperature. P alkaline peroxide stage, Paa peracetic acid stage. Ref without hot water treatment.**

| Treatment temperature °C | Ref | 70 | 120 | 130 | 150 |
|---|---|---|---|---|---|
| Brightness, % ISO | 70.5 | 72.0 | 75.9 | 73.1 | 70.3 |
| SR | 28.0 | 37.5 | 42.0 | 44.5 | 38.0 |
| Grammage, g/m$^2$ | 54.1 | 67.2 | 64.7 | 66.2 | 66.0 |
| Thickness, $\mu$m | 93.2 | 98.2 | 105 | 93.2 | 93.5 |
| Apparent density, g/cm$^3$ | 688 | 684 | 614 | 710 | 706 |
| Bulk, cm$^3$/g | 1.45 | 1.46 | 1.63 | 1.41 | 1.42 |
| Roughness, ml/min | 2909 | 1360 | 2569 | 1965 | 1513 |
| Air permeance, ml/min | 58.7 | 42.0 | 31.0 | 65.4 | 50.7 |
| Tensile index N.m/g | 63.4 | 69.8 | 70.8 | 77.2 | 72.4 |
| Tensile stiffness index, MN.m$^2$/kg | 6.24 | 6.82 | 7.26 | 6.61 | 6.36 |
| Stretch, % | 2.87 | 2.61 | 2.44 | 3.60 | 3.80 |
| Tensile energy, mJ/g | 1239 | 1209 | 1179 | 1835 | 1850 |
| Burst index, kPa.m$^2$/g | 4.55 | 5.04 | 4.74 | 5.62 | 5.53 |
| Tear index, mN.m$^2$/g | 4.7 | 4.7 | 5.0 | 3.1 | 5.5 |

tion could be notably reduced. The possibilities for developing the hot water treatment process further, are either to minimise the consumption of sodium hydroxide in bleaching or to produce papermaking fibres without bleaching.

## Mechanical refining after hot water treatment

One option to minimise the use of chemicals in the process is to implement a mechanical refining stage after hot water treatment. The idea of the process is to produce both fibres for packaging material, as well as raw material for energy production, in the form of fines or dissolved solids.

As discussed earlier, due to the moderate conditions, only 10% of original wheat straw material dissolves during hot water treatment at 120°C temperature.

Mechanical refining produces a coarse fraction above 16 and 30 mesh, fibre fraction above 100 mesh and coarse fines above 200 mesh, as well as fines below 200 mesh. Figure 7 presents the photographs and Figure 8 the microscope pictures of these Bauer McNett fractions.

For each separate refining trial, the different fractions appeared the same, with only the amount of the fraction varying. The 16 mesh fraction consists of long bundles of fibres. The 30 mesh fraction consists of the same kind of bundles, but shorter. The 100 mesh fraction consists of separate fibres but also some smaller bundles of fibres can be seen. The 200 mesh fraction consists of shorter fibre pieces.

The amount of fines, measured using the Bauer McNett method, is the difference between the amount of input pulp and the sum weight of the other fractions. During the fractionation some fibre losses may occur and therefore this method can only be used to estimate the fines level.

## Refining time

Figure 9 shows the effect of refining time on Bauer McNett fractions. When increasing the refining time, the amount of the coarse fraction above 16 mesh reduces and the amount of the fibre fraction increases as expected. However, the difference between 90 and 120 s refining time is modest. The average fibre length of the 90 s refining time, 100 mesh fraction, was 0.90 mm and 120 s refining time 0.92 mm respectively.

## Coarse fraction refining

When the coarse fraction was refined again the relative proportion of fibre fraction and coarse fines increased compared to the initial refining of straw, but still the amount of fine fines below 200 mesh was not increased (Fig. 10). The average fibre length of the 150 s refining time, 100 mesh fraction, was 0.95 mm. Therefore it is possible to return the coarse fraction to refining and thus increase the fibre fraction. Figure 11 shows the estimate of the Bauer McNett fractions if the coarse fraction is returned to refining 3 times,

**Fig. 7** **Photographs of the Bauer McNett fractions. Refining of hot water treated wheat straw with VTT Wing refiner, refining time 90 s.**

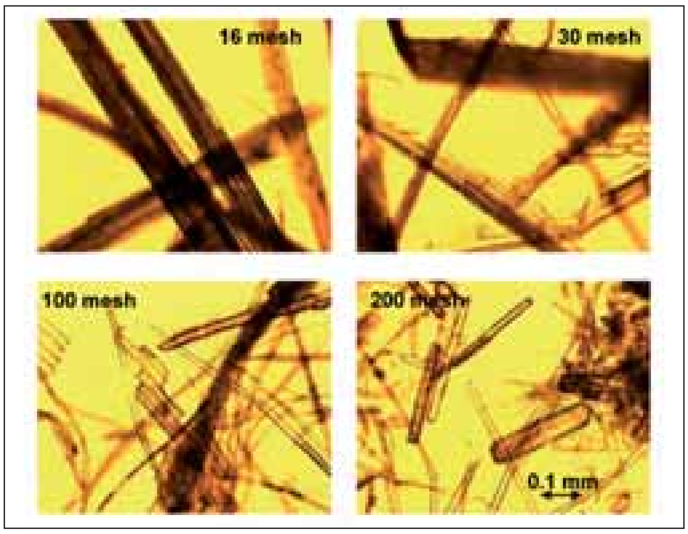

**Fig. 8** **Microscope pictures of the Bauer McNett fractions. Refining of hot water treated wheat straw with VTT Wing refiner, refining time 120 s.**

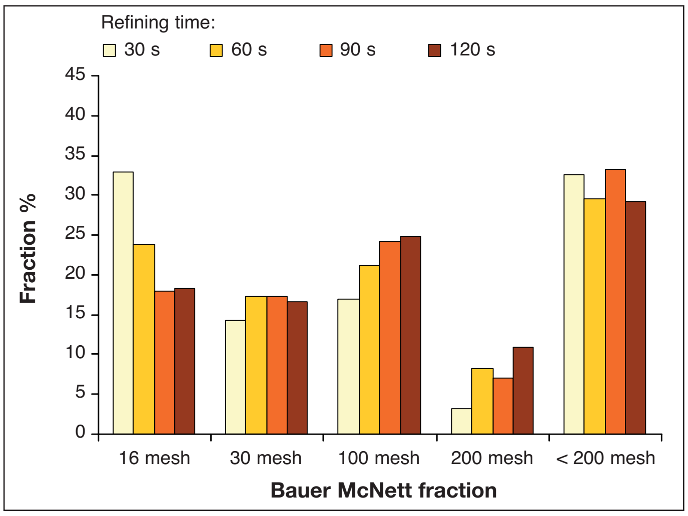

**Fig. 9** **Effect of refining time on Bauer McNett fractions. Refining of hot water treated wheat straw with VTT Wing refiner.**

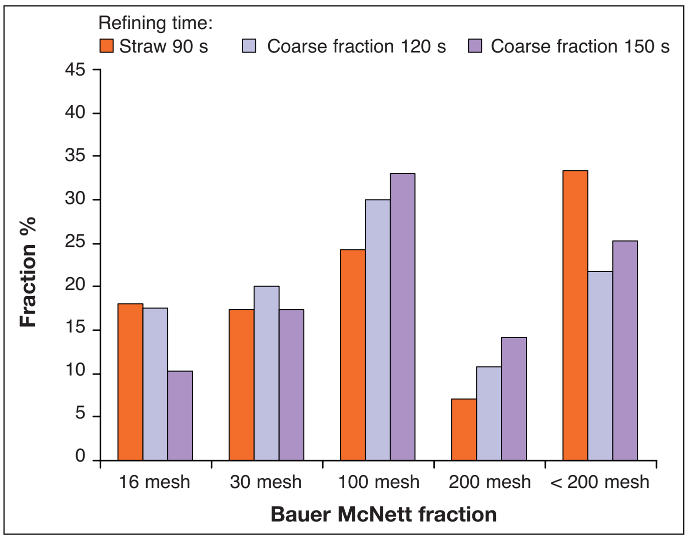

**Fig. 10** **Effect of refining time on Bauer McNett fractions. Refining of wheat straw coarse fraction with VTT Wing refiner.**

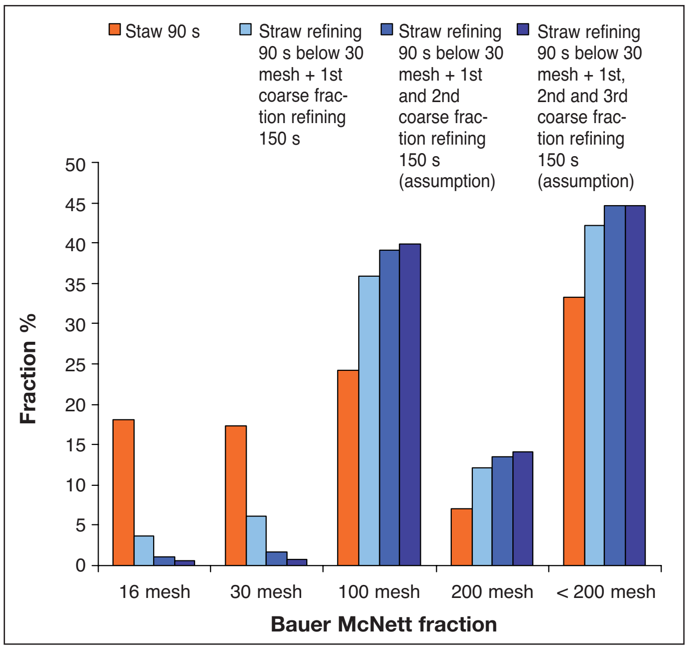

**Fig. 11** **Return of coarse fibre fraction to refining, mass balance of Bauer McNett fractions. Refining of hot water treated wheat straw and coarse fibre fraction with VTT Wing refiner.**

assuming it is refined equally each time.

### Mass balance

These mechanical refining experiments suggest that it is possible to produce about 54% fibres for paper production and 46% of fines to be used in energy production. If the hot water treatment yield is taken into account the fibre fraction to paper production is 49% of the original straw and fines fraction to energy production 41%. By altering the refining conditions it would be possible to increase the proportion outgoing to energy production.

### Potential paper properties of mechanically refined wheat straw pulps

Because the fractions of separate refinings looked the same, selected wheat straw pulps were wet disintegrated and fractionated with Bauer McNett apparatus. 100 mesh and 200 mesh fractions were combined and the paper technical properties were analysed for this pulp mixture. The average fibre length of this pulp was 0.67 mm. The paper technical properties of wheat straw pulp and wheat straw/softwood mixture pulp are presented in Table 4.

The strength properties, especially the tensile strength, of the produced wheat straw pulp are very poor while the drainability is good. Scott Bond bonding strength is also quite low. If the straw pulp is mixed with a pulp of better quality, the amount of straw pulp could be between 20% and 40%, especially if the other pulp were beaten to higher tensile strength. The addition of wheat straw pulp impairs the surface and optical properties and thus the printability. This kind of wheat straw pulp with high bulk could perhaps be used as a raw material for the middle layer of a board when mixed with a pulp of better strength properties, or for moulded fibre packages as such.

### Potential paper properties of chemically treated, mechanically refined wheat straw pulps

The strength properties of the wheat straw pulps can be improved, for instance by sizing or by a chemical treatment such as a bleaching stage. The properties of alkaline peroxide treated wheat straw pulp are presented in Table 5 and the properties of starch spray applied handsheets in Table 6. The pulp yield of the alkaline peroxide treatment was 89.7% and the bonding ability of mechanically refined wheat straw fibres was significantly improved in the treatment. The Scott Bond strength is quite reasonable, but the tensile index is still relatively low. The amount of the alkaline peroxide treated wheat straw pulp in a pulp mix could be clearly higher than the untreated wheat straw pulp amount.

The starch spraying also improves the strength properties. The straw quantity that could be used depends on the amount of added starch. With 1% starch application mechanical refined wheat straw pulp in the blend could be increased to 40% while maintaining the same tensile strength level. Similarly with 2% starch application the wheat straw amount could be increased to 50% in the pulp mix. The positive effect on bonding ability was even larger.

**Table 4.**
**Paper technical properties of wheat straw pulp and the wheat straw/softwood pulp mixtures. Hot water treatment of wheat straw at 120°C followed by mechanical refining. 100 and 200 mesh Bauer McNett fractions combined. Bleached and dried softwood (SW) mill pulp beaten 10 min with Valley.**

| | 100% Straw pulp | 80% Straw pulp/ 20% SW pulp | 60% Straw pulp/ 40% SW pulp | 40% Straw pulp/ 60% SW pulp | 20% Straw pulp/ 80% SW pulp | 100% SW pulp 10 min Valley beating |
|---|---|---|---|---|---|---|
| Brightness, % ISO | 24.7 | 26.6 | 29.8 | 34.6 | 44.4 | 95.1 |
| SR | 17.0 | 12.4 | 12.4 | 14.4 | 16.0 | 14.0 |
| Drainage time, s | 5.6 | 5.8 | 5.8 | 5.6 | 5.7 | 5.8 |
| Grammage, g/m$^2$ | 64.6 | 65.4 | 67.7 | 65.3 | 65.5 | 68.0 |
| Thickness, µm | 271 | 239 | 214 | 171 | 147 | 112 |
| Apparent density, g/cm$^3$ | 0.238 | 0.274 | 0.316 | 0.381 | 0.446 | 0.606 |
| Bulk, cm$^3$/g | 4.20 | 3.65 | 3.16 | 2.63 | 2.24 | 1.65 |
| Roughness, ml/min | 2620 | 2520 | 2530 | 2320 | 2210 | 1550 |
| Air permeance, ml/min | >3000 | >3000 | >3000 | >3000 | >3000 | 1680.0 |
| Tensile index N.m/g | 4.6 | 10.4 | 17.3 | 28.0 | 34.9 | 48.4 |
| Tensile stiffness index, MN.m/kg | 0.67 | 1.25 | 1.88 | 2.79 | 3.58 | 5.05 |
| Stretch, % | 1.5 | 2.0 | 2.7 | 3.2 | 3.4 | 3.4 |
| Tensile energy, mJ/g | 42 | 137 | 335 | 629 | 827 | 1143 |
| Burst index, kPa.m$^2$/g | 1.12 | 1.11 | 1.20 | 2.16 | 2.88 | 4.55 |
| Tear index, mN.m$^2$/g | 0.9 | 3.7 | 7.7 | 11.9 | 17.1 | 18.8 |
| Scott Bond J/m$^2$ | 44 | 56 | 72 | 97 | 120 | 188 |

**Table 5.**
**Paper technical properties of alkaline peroxide treated wheat straw pulp. Hot water treatment of wheat straw at 120°C followed by mechanical refining. 100 and 200 mesh Bauer McNett fractions combined. Alkaline peroxide treatment of straw pulp at 85°C. Chemical charges 5% NaOH, 4% $H_2O_2$, 0.25% $MgSO_4$, 0.2% DTPA.**

| | 100% straw pulp Alkaline peroxide treatment |
|---|---|
| Brightness, % ISO | 37.1 |
| Drainage time, s | 5.5 |
| Grammage, g/m$^2$ | 66.2 |
| Thickness, µm | 203 |
| Apparent density, g/cm$^3$ | 0.326 |
| Bulk, cm$^3$/g | 3.07 |
| Roughness, ml/min | 2760 |
| Air permeance, ml/min | >3000 |
| Tensile index N.m/g | 19.2 |
| Tensile stiffness index, MN.m/kg | 2.15 |
| Stretch, % | 2.1 |
| Tensile energy, mJ/g | 268 |
| Burst index, kPa.m$^2$/g | 1.36 |
| Tear index, mN.m$^2$/g | 2.8 |
| Scott Bond J/m$^2$ | 95 |

**Table 6.**
**Paper technical properties of starch sprayed wheat straw pulp / softwood pulp mix handsheets. Hot water treatment of wheat straw at 120°C followed by mechanical refining. 100 and 200 mesh Bauer McNett fractions combined. Bleached and dried softwood (SW) mill pulp beaten with Valley 10 min. Starch amount 1% and 2% of total weight.**

| | Starch amount, % of total weight | 100% straw pulp | 80% straw pulp/ 20% SW pulp | 60% straw pulp/ 40% SW pulp | 40% straw pulp/ 60% SW pulp | 20% straw pulp/ 80% SW pulp |
|---|---|---|---|---|---|---|
| Grammage, g/m$^2$ | 1 | | 65.0 | 68.7 | 66.8 | 64.6 |
| | 2 | 66.6 | 67.6 | 69.0 | 69.6 | 67.3 |
| Thickness, µm | 1 | | 252 | 239 | 192 | 161 |
| | 2 | 297 | 261 | 235 | 203 | 167 |
| Apparent density, g/cm$^3$ | 1 | | 0.258 | 0.287 | 0.348 | 0.402 |
| | 2 | 0.224 | 259 | 0.293 | 0.342 | 0.403 |
| Bulk, cm$^3$/g | 1 | | 3.88 | 3.48 | 2.87 | 2.49 |
| | 2 | 4.46 | 3.86 | 3.41 | 2.92 | 2.48 |
| Tensile index, N.m/g | 1 | | 17.2 | 25.3 | 39.3 | 47.5 |
| | 2 | 11.4 | 20.2 | 28.8 | 43.5 | 55.0 |
| Tensile stiffness index, MN.m/kg | 1 | | 1.78 | 2.57 | 3.58 | 4.46 |
| | 2 | 1.29 | 1.97 | 2.87 | 3.72 | 4.70 |
| Stretch, % | 1 | | 2.1 | 2.5 | 3.1 | 3.2 |
| | 2 | 1.6 | 2.1 | 2.3 | 3.3 | 3.7 |
| Tensile energy, mJ/g | 1 | | 238 | 468 | 859 | 1060 |
| | 2 | 103 | 294 | 474 | 984 | 1380 |
| Scott Bond J/m$^2$ | 1 | | 74 | 95 | 116 | 135 |
| | 2 | 69 | 99 | 109 | 149 | 186 |

## CONCLUSIONS

In producing a bleached straw pulp, a final brightness of ISO 75% could be reached by hot water treatment and subsequent peroxide bleaching, at a pulp yield above 50%. The pulp is well defibrated during bleaching.

The hot water treatment has a positive role in the process and the optimum temperature is about 100°C. Less than 10% of the original wheat straw material is dissolved during the hot water treatment below a temperature of 120°C. No acid addition is needed.

The peroxide bleaching can be performed without stabilisers because of the high magnesium and/or silica content of the wheat straw raw material.

Compared to soda cooked wheat straw

pulps, the potential paper properties of wheat straw pulps produced by hot water treatment and peroxide bleaching are equivalent or even superior, while the bleached yield is clearly higher.

The idea of hot water treatment is to avoid the need for chemicals recovery and its associated silica problems. However, at the current stage of research development the new process still consumes large amounts sodium hydroxide during bleaching, when the target brightness is ISO 75–80%. In practice this means, that the process would still need some kind of chemical recovery system unless bleaching chemical consumption could be reduced notably.

Without seeking a high brightness pulp, it is possible to produce a mix of suitable fibre raw materials for the paper industry and fines for energy production, by hot water treatment and subsequent refining. The amount of useful fibres is 49% of original raw material and the amount of fines 41% of original raw material. (10% of the original wheat straw material is dissolved during hot water treatment). It is possible to increase the amount of fines for energy production by altering the refining conditions.

Such a process is unique in its simplicity, the investment costs are moderate and the process chemical requirements low enough to make the recovery of chemicals unnecessary. The potential paper properties of the produced pulp are low but they can be improved for instance by sizing or by chemical treatment.

## ACKNOWLEDGEMENTS

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Paper III

# Alkaline peroxide bleaching of hot water treated wheat straw

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# ALKALINE PEROXIDE BLEACHING OF HOT WATER TREATED WHEAT STRAW

Suvi Mustajoki,[a] Anja Leponiemi,[a]* and Olli Dahl

The aim of this study was to evaluate the possibilities for chemical consumption reduction in P-P-Paa-P bleaching (P alkaline peroxide stage, Paa peracetic stage) of hot water treated straw and the effect of the wheat straw variability on the process. Papermaking fibre production from wheat straw using such a process could be implemented on a small scale if chemical consumption was low enough to eliminate the need for chemical recovery. The pulp properties obtained with this process are equal to or even superior to the properties of wheat straw soda pulp. The possibility of enhancing the first peroxide stage with oxygen and pressure was studied. The possibility for substitution of sodium hydroxide partially with sodium carbonate was also investigated. The objective was to achieve International Standardization Organization (ISO) brightness of 75%, with minimal sodium hydroxide consumption, whilst maintaining the pulp properties. The optimization of the peroxide bleaching is challenging if the final brightness target cannot be reduced. Results indicate that up to 25% of the sodium hydroxide could be substituted with sodium carbonate without losing brightness or affecting pulp properties. Another possibility is a mild alkali treatment between the hot water treatment and the bleaching sequence.

*Keywords: Non-wood fibre; Wheat straw; Biorefinery; Hot water treatment; Bleachability; Pulp properties*

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## INTRODUCTION

The conventional way to produce wheat straw pulp on a mill scale is through the use of the soda cooking method. Evaporation and recovery of spent alkaline cooking liquor is challenging because of the high silica content of wheat straw raw material. Silica dissolves in alkaline cooking and creates well-known, serious problems in the recovery area (Boman et al. 2009). In addition, soda cooking consumes a large quantity of sodium hydroxide; usually the NaOH charge is approximately 12 to 18%. Due to these difficulties of processability and poor process economics, there is a need for a process which overcomes these deficiencies (Feng et al. 2001). A hot water treatment, where wheat straw is treated with hot water for 60 min at 120˚C as a pretreatment before alkaline peroxide bleaching, is an option for wheat straw pulping. This treatment initiates a better bleachability of the straw pulp. The actual defibration of straw then occurs during the following bleaching (Leponiemi et al. 2010). Using sodium hydroxide for adjusting the conditions in alkaline peroxide bleaching is very effective, since it is a strong base. Due to the high alkalinity, however, sodium hydroxide dissolves carbohydrates, especially hemicelluloses, from pulp, which in turn has a negative impact on the pollution load of the waste water treatment plant. Thus, replacing sodium hydroxide by a weaker alkaline compound could help to minimize carbohydrate dissolution while preserving high bleachability (Li et al. 2004).

Pan and Leary (2000) proposed sodium carbonate as an alkali source for alkaline peroxide mechanical pulping (APMP) of wheat straw. The achieved brightness and strength properties were lower as compared to the use of sodium hydroxide, but resulted in higher pulp yield and thus lower chemical costs and lower chemical oxygen demand (COD) content of spent bleaching liquors. In the APMP process the choice between NaOH and $Na_2CO_3$ is based on the target brightness and applied peroxide charges. The use of sodium carbonate is preferred when the peroxide charge is relatively low, e.g., about 4% on straw dry matter. In this case similar brightness levels can be achieved with $Na_2CO_3$ as compared to NaOH with lower peroxide consumption.

Earlier studies have shown that a hot water treatment followed by alkaline peroxide bleaching offers an interesting avenue in the search for non-wood pulping alternatives with potential to address the need for simple and economically competitive small scale pulping processes for non-wood materials. The process consumes high amounts of sodium hydroxide in bleaching with the target brightness of 75 to 80% ISO. In practice this means that the process would need some kind of chemical recovery system, unless the bleaching chemical consumption could be notably reduced (Leponiemi et al. 2010). The aim of this study was to use this simple and non-traditional process to produce chemical type wheat straw pulp with brightness of 75% ISO, instead of traditional fully bleached chemical pulp. Furthermore, the aim was to evaluate the possibilities for chemical consumption reduction in P-P-Paa-P bleaching and the effect of the wheat straw variability on the process. Since glucose and xylose are already present in the hot water treatment filtrate, they may result in additional chemical consumption or otherwise reduce the following peroxide bleaching performance. The variation in raw material was studied by comparing straws grown during different years. The objective was to achieve a brightness of 75% ISO, with minimal sodium hydroxide consumption, whilst maintaining the pulp properties. The variables studied were the pressurisation of the first peroxide ($P_1$) stage with oxygen, the substitution of sodium hydroxide partially with sodium carbonate, and a mild alkali treatment before the actual peroxide bleaching. In addition, the role of sugars in the bleaching stages was studied by adding glucose or xylose to the $P_1$ stage.

## EXPERIMENTAL

### Raw Material

The raw material used was air-dried wheat straw, which was cultivated by MTT (Agrifood Research Finland) and harvested during the summers of 2006 and 2007. The 2006 straw (06Straw) was chopped with a bale chopper in the winter of 2006-2007. The 2007 straw (07Straw) was chopped at the end of the threshing machine, air dried, and stored in room temperature (1st batch). Furthermore, a second batch of 07Straw was stored in an unheated barn for about two years.

The straws were screened using screens with 6 and 7 mm diameter holes. Oversized and fines fractions were removed. The standard screening method SCAN-CM 40:88 was followed with the exception of screens and the screening time, which was 30 s. The dry matter content of screened straw was determined according to the standard SCAN-CM 39:88.

## Raw Material Analysis

The amount of acetone extractives was determined according to SCAN-CM 49:93. Total lignin content of the raw material was analyzed according to KCL analyzing method No. 115B:82. Quantitative determination of straw carbohydrates was implemented by total acid hydrolysis according to Sjöström et al. (1969) and Janson (1970). The monosaccharides as their alditol acetate derivates were separated by gas chromatography using a capillary column NB-1701 and an isothermic program. The oven temperature was 210°C and the temperature for injector and detector 260°C.

Ash and multi-element determination of raw material started with drying the samples at 105°C and grinding them with a hammer mill. Then the samples were ground again with a Fritsch pulverisette grinder, dried at 105°C, and ashed at 550°C for 12 hours. For multi-element analysis the samples were dissolved by hydrogen fluoride-nitric acid. These solutions were analyzed with ICP-MS technique for multi-element contents.

## Hot Water Treatment

Hot water treatment was implemented with an air heated rotating serial digester including six 2.5L autoclaves. Hot water treatment conditions are presented in Table 1.

**Table 1.** Hot Water Treatment Conditions

| | |
|---|---|
| Temperature (°C) | 120 |
| Time (min) | 60 |
| Water:straw ratio | 10:1 |
| DTPA (% on straw) | 0.2 |

The autoclaves were filled with the pre-determined amount of screened straw. Only then, water and DTPA were charged after thorough mixing. The target temperature of 120 ºC was kept constant during the whole hot water treatment. These conditions were kept constant throughout all test runs.

The aqueous filtrate samples were stored for further analysis. Straw washing was performed by diluting the treated straw with deionised water, agitating, then leaving the mixture to settle for 2 minutes followed by removal of the excess water through a wire pouch. Dilution and thickening was repeated 3 times. Finally, the treated straw was centrifuged to ~25% consistency.

## Reference Bleaching

The unpressurised bleaching stages were carried out in polyethylene bags in a water bath. Chemical charges were calculated on the initial amount of the straw. The bleaching conditions for the reference pulps and for the all other experiments, including reaction time, reaction temperature, and chemical dosage, are presented in Table 2.

**Table 2.** Bleaching Conditions of Reference, Pressurised $P_1$, Sugar Addition and Alkali Pretreatment Pulps. Consistency 10%, Temperature in $P_2$, Paa and $P_3$ stages 85˚C and, Time in $P_2$ and $P_3$ Stages 180 min and in Peracetic Acid Stage 60 min. Hot Water Treatment at 120°C Followed by P-P-Paa-P Bleaching. $PP_1$=Pressurised $P_1$ Stage, APT=NaOH Pretreatment and PPT= $O_2$ Pressurised NaOH Pretreatment.

| | | Reference bleaching | | Pressurised $P_1$ | | | Sugar addition | | | Alkali pretreatment | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Low chem | High chem | $PP_1$ 95°C 120 min | $PP_1$ 105°C 60 min | $PP_1$ 105°C 120 min | Low chem sugar | Medium chem sugar | High chem sugar | APT 2% NaOH | APT 2.5% NaOH, seq. P-Paa-P | PPT 3% NaOH shorter time | PPT 3% NaOH longer time | PPT 4% NaOH |
| Alkaline pretreat-ment | Pressure (bar) | - | - | - | - | - | - | - | - | - | - | 3 | 3 | 3 |
| | Time (min) | - | - | - | - | - | - | - | - | 180 | 240 | 60 | 90 | 90 |
| | NaOH (%) | - | - | - | - | - | - | - | - | 2.0 | 2.5 | 3.0 | 3.0 | 4.0 |
| $P_1$ | NaOH (%) | 7.0 | 8.5 | 6.0 | 6.0 | 6.0 | 7.0 | 8.0 | 8.5 | 3.5 | 2.5 | 3.0 | 3.0 | 3.0 |
| | $H_2O_2$ (%) | 4.0 | 5.0 | 4.0 | 4.0 | 4.0 | 4.0 | 5.0 | 5.0 | 3.0 | 3.0 | 2.0 | 2.0 | 2.0 |
| | Temperature (°C) | 85 | 85 | 95 | 105 | 105 | 85 | 85 | 85 | 85 | 85 | 85 | 85 | 85 |
| | $O_2$-pressure (bar) | - | - | 3 | 3 | 3 | - | - | - | - | - | - | - | - |
| | Time (min) | 60 | 60 | 120 | 60 | 120 | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 |
| | $MgSO_4$ (%) | - | - | 0.3 | 0.3 | 0.3 | - | - | - | - | - | - | - | - |
| | DTPA (%) | - | - | 0.2 | 0.2 | 0.2 | - | - | - | - | - | - | - | - |
| | Sugar (mg/L) | - | - | - | - | - | 150 | 150 | 150 | - | - | - | - | - |
| $P_2$ | NaOH (%) | 1.0 | 1.5 | 1.5 | 1.0 | 1.0 | 1.0 | 1.0 | 1.5 | 0.75 | - | 0.5 | 0.5 | 0.5 |
| | $H_2O_2$ (%) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | - | 2.0 | 2.0 | 2.0 |
| Paa | NaOH (%) | 0.2 | 0.2 | 0.2 | 0.5 | 0.5 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| | Peracetic acid (%) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| $P_3$ | NaOH (%) | 1.0 | 1.5 | 1.0 | 1.0 | 1.0 | 1.0 | 1.5 | 1.5 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 |
| | $H_2O_2$ (%) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Acidifi-cation | $SO_2$ (%) | 0.7-0.8 | 1.1 | 1.1 | 0.7 | 0.9 | 0.4 | 0.7 | 0.6-0.7 | 0.5 | 0.5 | 0.5 | 0.4 | 0.4 |

After each bleaching stage the pulp was washed by the dilution and thickening method, as explained above. After the last bleaching stage and wash, the pulp was acidified. The pulp was diluted with deionised water, and diluted sulphuric acid was added until the pH reached roughly 3.8. After 15 minutes, the final pH was 4 to 4.5. After acidification the pulp was washed again, as explained before.

The pulps were weighed, and dry matter content determined to define the yield after each stage. When calculating the bleaching chemical dosages for the following bleaching stage, it was assumed that there were no yield losses. Only the amount of the pulp used for defining dry matter content and ISO brightness were deducted from the original amount of pulp. However, the yield losses were taken into account when calculating the bleaching consistency.

## Pressurised $P_1$

The pressurised $P_1$ stage was equipped with an air heated rotating serial digester using 2.5 litre autoclaves. $O_2$-pressure was 3 bars in all pressurised bleaching trials and the temperature was 95°C or 105°C. The temperature rise during heat-up period from 80°C was approximately 1°C per minute. The reaction time was 60 or 120 minutes. The conditions of the pressurised $P_1$ stages and the following bleaching are presented in Table 2. After bleaching the autoclaves were handled as explained in hot water treatment part.

## Carbonate Bleaching

In each bleaching stage 25, 32.5, or 40% of total alkali was replaced with $Na_2CO_3$. The bleaching conditions were the same as in the higher chemical dosage reference bleaching.

## Sugar Addition Bleaching

D(+)-glucose or D(+)-xylose was diluted in a small amount of deionised water and added to hot water treated 07Straw before chemical addition in the $P_1$ stage. The amount of added sugar was adjusted in order to raise the sugar level of the liquid filling of the $P_1$ stage. The ratio of the added sugar amount versus the total liquid filling of $P_1$ stage was 150 mg/L. The bleaching conditions of the sugar addition bleaching trials are presented in Table 2.

## Alkali Pretreatment

A mild alkali pretreatment was performed prior to the actual P-P-Paa-P bleaching. The alkali pretreatment stage was conducted similarly to peroxide stages excluding the peroxide addition. Table 2 presents the bleaching conditions.

## Screening

Pulps were screened after bleaching with a Valmet TAP03 screen with 0.25mm screen openings or with a flat screen with 0.25mm screen openings. Before screening, pulps were wet disintegrated according to standard ISO 5263, except for the number of the revolutions, which was approximately 10,000. For the second batch of pulps, the number of revolutions was 30,000.

After disintegration the pulp was diluted with deionised water to about 1%

concentration and screened. After screening, reject and accept fractions were recovered in their own containers.

Accepts from the screening were centrifuged, homogenized, and the dry matter content was determined according to standard SCAN-C 3:78. The homogenized accepts were wet disintegrated again for sheet preparation according to ISO 5263 after the dry matter determination, except that the number of revolutions was approximately 2000. The screened accepts from the flat screen were stored as slush for sheet preparation for each of the pulps. The rejects were dried in an oven and weighed. The reject proportion was calculated as a percentage of bone dry pulp.

## Pulp and Liquid Analysis

Pretreated straw samples were weighed, and their dry matter content was determined from each test point according to standard SCAN-C 3:78 to define the yield after hot water treatment. The ISO brightness after each bleaching stage was measured according to standard SCAN-C 11:75.

The carbohydrate content of selected hot water treatment and $P_1$ stage filtrate samples was analyzed by methanolysis according to Holmbom and Örså (1993). The gas chromatographic analysis was performed with a Hewlett-Packard 5890 gas chromatograph using a NB-30 capillary column (25 m * 32 mm I.D.). The temperature program was the following: 2 min in 100°C, 4°C/min to 200°C, and 2 min at 200°C. About 1 μL of the sample was injected via split injector (260°C) with a split ratio of 1:20. Hydrogen was used as a carrier gas, and the FID detector temperature was 290°C. The total amount of dissolved carbohydrates in the hot water treatment or bleaching filtrate was calculated based on the hot water treatment/bleaching consistency and the amount of carbohydrates in filtrate.

Filtrate samples from hot water treatment and selected bleaching stages were analyzed for organic acid anions with ion chromatograph Dionex ICS1500 and the IonPac AS9-HC column. Filtrate samples were filtered with 0.45μm filters and diluted to 100th part. The eluent was 9.0 mM $Na_2CO_3$, and the eluent flow rate was 1.0 mL/min. The acetate level (% on straw) was calculated based on the acetate content, which was determined via filtrate analysis with a Dionex ICS-1500 (column AS 9HC).

## Paper Technical Properties

The Schopper Riegler number was determined according to standard SCAN-C 19:65. Laboratory sheets were prepared according to standard SCAN-CM 26:76. The target grammage was 60g/m$^2$. Sheets were dried between blotters in a temperature and air moisture conditioned room maintained at 23°C and with 50% relative humidity. After conditioning, the laboratory sheets were cut to 141 x 141mm sheets with a punching knife.

All paper technical properties were determined according to ISO or SCAN standard methods.

## RESULTS AND DISCUSSION

### Chemical Composition

Table 3 presents the chemical composition of the wheat straws used in the experiments. The total amount of sugars was over half of the wheat straw raw material, with glucose as the main component. The 06Straw had somewhat greater glucose, xylose, and arabinose share, and thus higher total sugar content than the 07Straw. The total lignin content of the 06Straw was lower than that of the 07Straw, but the soluble lignin amount was nearly the same, and the extractives content was somewhat higher in the 06Straw.

The 06Straw contained approximately 3% units less ash than the 07Straw. The amount of ash could influence ISO brightness and chemical consumption in the bleaching. Higher ash content of the 07Straw can explain part of the difference in Klason lignin. All the ash is not dissolved during acid hydrolysis, thus the undissolved part of it may be seen as somewhat increased gravimetric lignin content. The ash substances can accumulate on the fibre surfaces during bleaching and sheet preparation and therefore decrease brightness. Ash also contains metal ions, which can cause peroxide decomposition and increase the consumption of bleaching chemicals and therefore decrease bleachability.

**Table 3.** The Chemical Composition of Wheat Straw Raw Materials, Hardwood and Softwood.

| | 06Straw | 07Straw | Hardwood (Alen 2000; Sixta et al. 2006) | Softwood (Alen 2000; Sixta et al. 2006) |
|---|---|---|---|---|
| Glucose (%) | 38.4 | 36.6 | 38.3-51.3 | 33.0-41.7 |
| Xylose (%) | 20.1 | 17.4 | 15.1-24.9 | 3.3-7.6 |
| Rhamnose (%) | 0.2 | 0.1 | 0.5-0.6 | 0.0-0.3 |
| Arabinose (%) | 3.0 | 2.4 | 0.4-1.0 | 1.0-2.0 |
| Mannose (%) | 0.4 | 0.5 | 0.9-3.8 | 8.1-13.6 |
| Galactose (%) | 0.8 | 0.8 | 0.7-1.4 | 1.0-6.1 |
| Total sugar (%) | 62.9 | 57.8 | 66.0-74.4 | 54.4-65.2 |
| Gravimetric lignin (%) | 23.3 | 26.6 | - | - |
| Total lignin | | | 20.8-25.4 | 26.8-32.1 |
| Extractives (%) | 2.1 | 1.3 | 1.2-4.6 | 1.7-5.3 |
| Ash (%) | 6.8 | 9.7 | 0.3-1.5 | 0.3-1.5 |
| Magnesium (mg/kg) | 1200 | 1000 | 11-320 | 41-270 |
| Silica (mg/kg) | 19900 | 25600 | 10-100 | 10-100 |
| Manganese (mg/kg) | 11.9 | 13.4 | 2-250 | 25-440 |
| Iron (mg/kg) | 96.3 | 124.0 | 11-12 | 6-14 |
| Copper (mg/kg) | 3.5 | 3.4 | <5 | <5 |

The 07Straw had a clearly higher silica content compared to the 06Straw. Wet growing conditions are known to affect the amount of silica, for instance in the case of rice straw. Indeed, the summer of 2006 was very dry and the summer of 2007 was very rainy. Compared to wood, the silica and magnesium content of wheat straw is very high. The 07Straw contained somewhat smaller quantities of magnesium than the 06Straw. Wood contains only 10 to 100mg/kg silica and 10 to 320mg/ kg magnesium (Alen 2000; Sixta et al. 2006). The 07Straw contained slightly more harmful metals such as iron and manganese than did the 06Straw. Compared to wood, the iron content of wheat straw is high but the manganese content is low. One of the most important factors for successful peroxide bleaching is a relatively high magnesium / manganese molar ratio. The magnesium / manganese molar ratio for the 06Straw was 228 and 169 for the 07Straw. Both of these values exceed the appropriate level, which is over 100 (Basta et al. 1994; Lindeberg 1994).

Table 4 presents the acetate analysis results for the selected reference filtrates, performed after the hot water treatment and bleaching stages. The 06Straw was bleached with only the lower chemical dosage reference conditions, and the 07Straw was bleached with both the lower and higher chemical dosage reference conditions.

**Table 4.** Acetate Amount Analyzed from the Filtrates after Hot Water Treatment and Bleaching Stages in the Case of Reference Bleaching Conditions.

| | Acetate amount (% of original straw) | | |
|---|---|---|---|
| | 06Straw Low Chem. | 07Straw Low Chem. | 07Straw High Chem. |
| Hot water treatment | 0.3 | 0.4 | 0.4 |
| $P_1$ | 2.1 | 2.1 | 2.4 |
| $P_2$ | 0.1 | 0.2 | 0.2 |
| Paa | 1.2 | 0.7 | 0.7 |
| $P_3$ | 0.1 | 0.1 | 0.2 |
| Total | 3.8 | 3.5 | 3.9 |

The total amount of acetate in hot water treatment and bleaching filtrates was somewhat higher from the 06Straw than from the 07Straw with the same bleaching conditions. Slightly more acetate was released during the hot water treatment from the 07Straw but less during the bleaching compared to the 06Straw. The main part of the acetate was released in the first peroxide stage, where the sodium hydroxide charge was highest, as expected.

The acetate released during hot water treatment was in the form of acetyl groups still attached to the xylan oligomers and as free acetate/acetic acid. The results in Table 4 describe the free acetate content of the extracts. The difference between the xylan concentration in the hot water treatment extracts of these two straws was very small (see Fig. 1). Similarly, the difference in free acetate content was also very small.

The amount of acetate released from the peracetic acid stage of the 06Straw was high compared to that of the 07Straw. The amount of released acetate from the $P_2$ and $P_3$ stages was quite low because of the low chemical charges. Increasing the sodium hydroxide charge in the bleaching increased the amount of acetate released as expected. Figure 1 presents the carbohydrate composition of the hot water treatment filtrate from the 06Straw and the 07Straw.

Hot water treatment removed twice the amount of carbohydrates from the 07Straw as from the 06Straw, but the amount of dissolved carbohydrates was still quite low. Most of the difference became from the amount of glucose and mannose released during hot water treatment.

## Reference Bleaching

The reference bleaching results showed that the 06Straw was bleached more easily with similar chemical charges and required less bleaching chemicals to reach 75% ISO brightness than the 07Straw. The difference in bleachability of the straws was seen after all bleaching stages. Figure 2 shows how brightness of the reference pulps developed during bleaching. Final brightness after $P_3$ and acidification was 5 to 8% ISO units higher for the 06Straw than for the 07Straw. The variation of separate bleachings has been tested earlier, and the repeatability of the obtained results is very good. The final brightness may vary only by max. 0.5%. Therefore the differences in final brightness above 1% can be considered as a tangible difference.

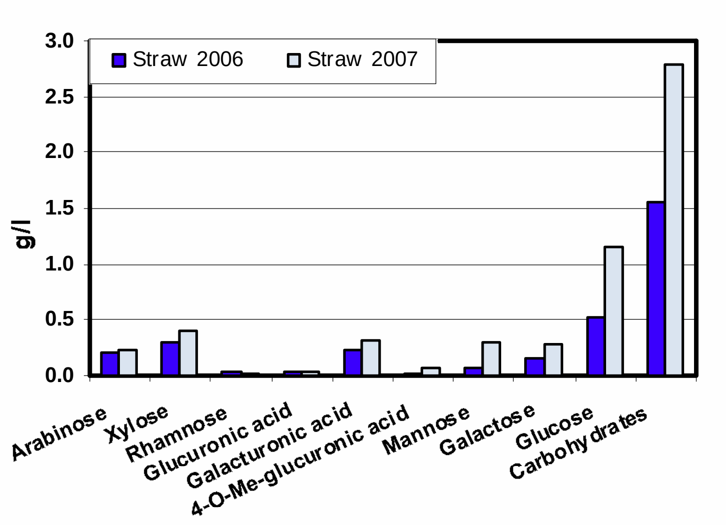

**Fig. 1.** Sugar content of hot water treatment filtrate from 06Straw and 07Straw by methanolysis as g/l

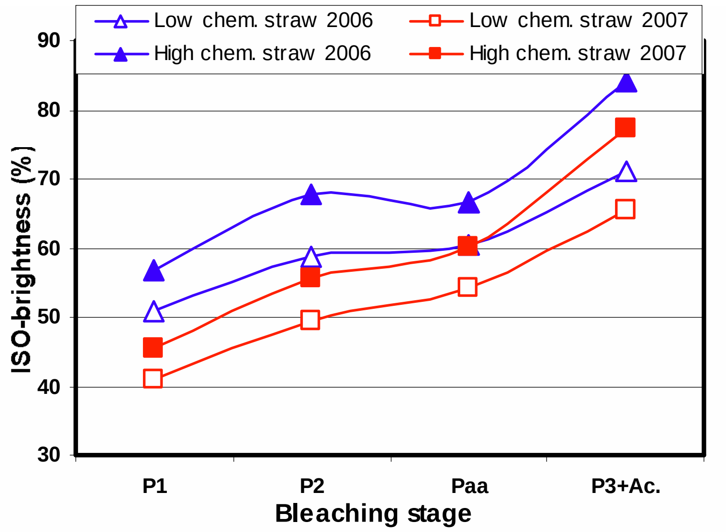

**Fig. 2.** Brightness of reference pulps after each bleaching stage. Raw material wheat straw 2006 and 2007. Hot water treatment of straw at 120°C for 60 min followed by P-P-Paa-P bleaching.

Figure 3 illustrates the reflectance values of the higher chemical charge reference bleaching of the hot water treated 07Straw. Compared to the pulp from the 06Straw, the pulp from the 07Straw had a clear decline and increment in the wavelength area 640 to 700nm. The drop was approximately 5% units from the level before and after the decline. When the bleaching proceeded from one stage to another, the reflectance decline decreased. The same decline was observed in all 07Straw bleaching trials. The 07Straw required a higher amount of bleaching chemicals than the 06Straw to defibrate and reach 75% ISO brightness. The difference between the 06Straw and the 07Straw chemical consumption could at least be partially explained by this difference in reflectance. The reflectance decline at the end of the measured wavelength area could mean that greyish/brownish components, possibly caused by finely dispersed inorganic deposits, exist in the pulp. Still, the possible components causing this decline in reflectance could not be identified.

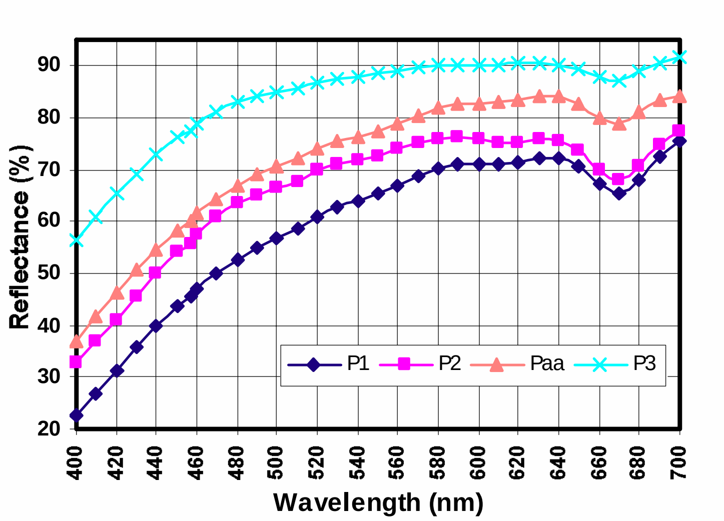

**Fig. 3.** Reflectance of higher chemical dosage pulp after each bleaching stage. Hot water treatment of the 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching.

Figure 4 presents the yield of the reference bleachings after each bleaching stage of sequence P-P-Paa-P. The pulps with the lowest chemical dosage had the highest yield, as expected. Generally a yield level above 50% is considered to be advantageous. The yield reduction in the alkaline peroxide bleaching results from the dissolution of carbohydrates and ash, but also lignin is partly dissolved. Kappa number of the bleached reference pulps was 33 for the lower chemical charge bleaching and 15 for the higher chemical charge bleaching, while no significant difference was seen between the 07Straw and 06Straw. The pulp yield from the 06Straw was higher compared to the pulp from the 07Straw with the same chemical dosages. The pulp from the 07Straw showed a yield exception in the $P_1$ stage, which was most probably due to an error in dry matter content determination. The yield measurement is not as reproducible as the brightness but differences above 1-2% can be considered as an actual difference.

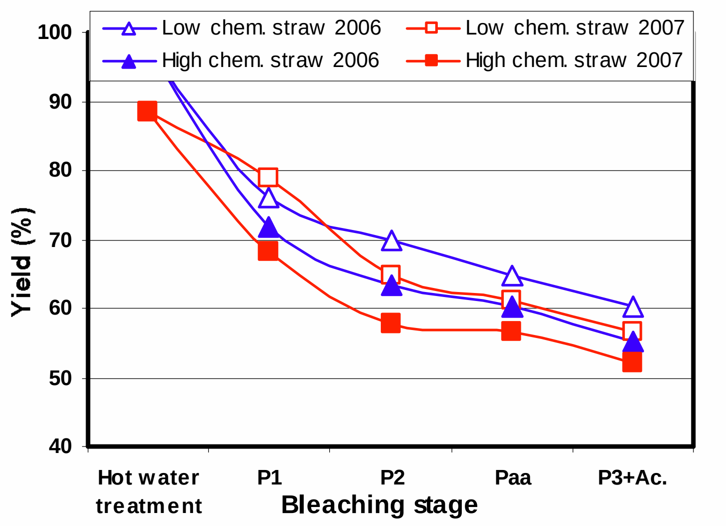

**Fig. 4.** Yield of reference pulps after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching.

In an addition to the chemicals and the process, storage also had an effect on the pulp bleachability of the hot water treated straw. Figure 5 presents the ISO brightness of the reference pulps produced from the 07Straw after each bleaching stage. This straw was stored in two different environments: The 1st batch was stored at room temperature for approximately half a year, and the 2nd batch was stored in an unheated barn for about two years, during which time the WeatherOnline service recorded that minimum and maximum temperatures were -17 and +29°C. The longer storage time and the influence of climate may have impaired the bleachability and the bleached pulp yield (Fig. 5 and Table 6).

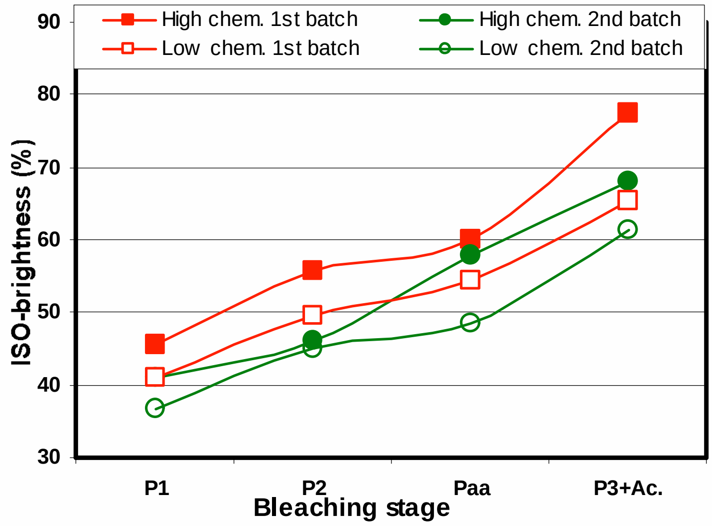

**Fig. 5.** Effect of storage on brightness after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching. 1st straw batch stored half a year in room temperature. 2nd straw batch stored in an unheated barn for two years.

The paper technical properties of the hot water treated and peroxide bleached wheat straw pulps were relatively good. Table 5 presents the paper technical properties of the reference pulps as well as all the other bleaching trials. The pulp properties obtained were equal to or even better than the properties of wheat straw soda pulp (Leponiemi et al. 2010). The reference pulp from Straw06 had higher ISO brightness, higher light scattering coefficient, higher tensile index, higher tear index, and lower bulk than the reference pulp from Straw07 with the same bleaching conditions. This indicates that the fibres from Straw06 were probably more bonded than the fibres from Straw07.

The storage of straw in an unheated barn impaired the optical properties of the bleached pulp. The light scattering coefficient was slightly lower, as was light absorption, but opacity remained at the same level. The Schopper Riegler number of the pulp that was produced from the outside-stored straw was higher than the SR from the inside-stored straw. The bulk of these pulps was also notably lower, and the tensile index higher. This indicates that the fines content and the bondability of the pulp produced from the 2nd batch straw was increased. This may, however, just be due to longer disintegration of these pulps and not because of the storage conditions.

## Pressurised $P_1$

$O_2$ pressure can be used to intensify alkaline peroxide bleaching, and because of the high chemical charges in the first P stage, it is advantageous to optimise the chemical consumption of this stage. Therefore the effect of pressurising the $P_1$ stage with oxygen was studied. Figure 6 illustrates the brightness of these bleachings after each bleaching stage, together with the reference pulp brightness. The raw material was from the first batch of 07Straw.

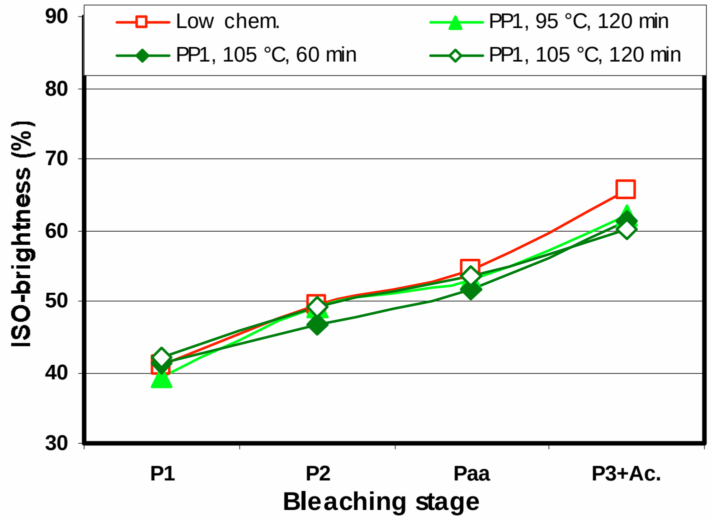

**Fig. 6.** Brightness of pressurised $P_1$ and reference bleachings after each bleaching stage. Hot water treatment of wheat straw (07Straw) at 120°C for 60 min followed by ($PP_1$)-P-Paa-P bleaching. $PP_1$ pressurised $P_1$ stage.

**Table 5.** Paper Technical Properties of Reference, Pressurised $P_1$, Sugar Addition and Alkali Pretreatment Bleaching Paper Sheets $PP_1$=Pressurised $P_1$ Stage, APT=NaOH Pretreatment and PPT= $O_2$ Pressurised NaOH Pretreatment.

| | Bleaching conditions | Straw batch | SR number | Grammage (g/m$^2$) | Thickness (µm) | Apparent density (kg/m$^3$) | Bulk (m$^3$/kg) | Opacity (%) | Light scatter (m$^2$/kg) | Light absorption (m$^2$/kg) | Tensile index (Nm/g) | Tear Index (Nm$^2$/kg) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reference bleaching | Low chem | 2006 | 32 | 58.5 | 93 | 629 | 1.52 | 71.6 | 23.9 | 0.7 | 63.4 | 4.6 |
| | High chem | 2006 | 30 | 60.8 | 96 | 636 | 1.53 | 70.3 | 23.1 | 0.5 | 62.4 | 4.4 |
| | Low chem | 1st | 32 | 59.0 | 88 | 668 | 1.54 | 71.1 | 22.4 | 0.8 | 55.9 | 3.9 |
| | High chem | 1st | 31 | 60.9 | 90 | 674 | 1.59 | 71.5 | 22.7 | 0.7 | 59.2 | 4.0 |
| | Low chem | 2nd | 34 | 71.8 | 112 | 639 | 1.56 | 69.7 | 19.7 | 0.3 | 63.9 | 3.6 |
| | High chem | 2nd | 43 | 83.9 | 113 | 743 | 1.35 | 71.2 | 18.8 | 0.2 | 69.8 | 5.4 |
| Pressurised $P_1$ | $PP_1$ 105°C 60 min | 1st | 32 | 64.8 | 109 | 592 | 1.69 | 76.0 | 24.9 | 0.8 | 48.7 | 3.9 |
| | $PP_1$ 105°C 120 min | 1st | 31 | 62.1 | 109 | 568 | 1.76 | 75.1 | 26.1 | 0.7 | 48.7 | 4.0 |
| Carbonate | High chem, 25 % $Na_2CO_3$ | 2nd | 30 | 67.5 | 99 | 683 | 1.47 | 68.6 | 21.4 | 0.3 | 58.0 | 4.4 |
| | High chem, 32.5 % $Na_2CO_3$ | 2nd | 29 | 67.7 | 97 | 696 | 1.44 | 67.9 | 18.4 | 0.3 | 57.8 | 4.6 |
| | High chem, 40 % $Na_2CO_3$ | 2nd | 32 | 68.5 | 101 | 679 | 1.47 | 70.5 | 21.5 | 0.4 | 57.8 | 4.6 |
| Sugar addition | Low chem, Gluc | 2nd | 47 | 67.9 | 102 | 669 | 1.50 | 69.5 | 18.8 | 0.4 | 60.3 | 4.7 |
| | Low chem, Xyl | 2nd | 42 | 67.6 | 99 | 680 | 1.47 | 68.7 | 18.8 | 0.4 | 63.2 | 4.3 |
| | Med. chem, Gluc | 1st | 31 | 65.2 | 97 | 675 | 1.48 | 70.7 | 22.6 | 0.4 | 71.1 | 4.2 |
| | Med. chem, Xyl | 1st | 35 | 65.7 | 97 | 681 | 1.47 | 67.9 | 20.9 | 0.3 | 70.0 | 4.4 |
| | High chem, Gluc | 1st | 31 | 64.3 | 93 | 689 | 1.45 | 74.7 | 28.2 | 0.4 | 60.0 | 4.5 |
| | High chem, Xyl | 1st | 55 | 66.9 | 100 | 672 | 1.49 | 70.0 | 21.9 | 0.4 | 73.8 | 3.9 |
| Alkali pretreat-ment | APT 2% NaOH | 2nd | 32 | 68.1 | 109 | 627 | 1.60 | 72.9 | 19.4 | 0.7 | 52.9 | 4.8 |
| | APT 2.5% NaOH P-Paa-P | 2nd | 57 | 68.3 | 112 | 609 | 1.64 | 78.2 | 19.0 | 1.4 | 50.8 | 3.4 |
| | PPT 3% NaOH, 60 min | 2nd | 49 | 68.7 | 107 | 644 | 1.55 | 74.9 | 18.6 | 0.9 | 53.5 | 4.7 |
| | PPT 3% NaOH, 90 min | 2nd | 30 | 67.7 | 107 | 684 | 1.46 | 71.6 | 18.3 | 0.6 | 57.0 | 5.3 |
| | PPT 4% NaOH | 2nd | 33 | 73.4 | 103 | 657 | 1.52 | 71.5 | 20.1 | 0.8 | 56.8 | 4.2 |

The pressurised $P_1$ stage was expected to intensify the peroxide bleaching and lower bleaching chemical consumption, especially that of NaOH. With the chosen, somewhat lower NaOH charge (6%), oxygen pressure in the $P_1$ stage did not give a clear advantage compared to the unpressurised bleaching; final brightness remained at about 3% units lower level than the reference. The NaOH charge of the reference pulp was somewhat higher. The best pressurised $P_1$ stage results were obtained at 95°C and 120 minutes reaction time.

Table 6 presents the yield of the pulps from the pressurised $P_1$ bleaching. All pulps with 6.0% NaOH charge in the $P_1$ stage arrived at nearly the same total yield. The yield level of the pressurised $P_1$ pulps was somewhat higher than the yield of the reference pulp. Due to the lower chemical concentration and shorter reaction time, less substances were dissolved during the pressurised $P_1$ stage than from the unpressurised stage. Despite of the higher yield level, the pulps defibrated properly. By pressurizing the first peroxide stage it was possible to reduce the NaOH charge by only about 1%.

The paper technical properties of the pressurised $P_1$ bleachings are presented in Table 5. The oxygen pressure in the $P_1$ stage and the lower chemical charge compared to the reference bleaching mostly affected the strength properties. The tensile index and the tear index of the pressurised $P_1$ bleaching sheets were slightly lower than those of the reference pulp. The bulk of the pulp from the pressurised bleachings was higher, which together with strength properties, is an indication of lower fibre bonding.

**Table 6.** Yield of Reference, Pressurised $P_1$ and Sugar Addition Bleachings after Each Bleaching Stage.

| | | | Yield (% of original straw) | | | | |
|---|---|---|---|---|---|---|---|
| | Bleaching conditions | Straw batch | Hot water treatment | $P_1$ | $P_2$ | Paa | $P_3$+Ac. |
| Reference bleaching | Low chem | 2006 | 97.7 | 76.0 | 70.0 | 64.8 | 60.4 |
| | High chem | 2006 | 97.7 | 71.9 | 63.5 | 60.4 | 55.3 |
| | Low chem | 1st | 88.3 | 78.9 | 64.8 | 61.0 | 56.6 |
| | High chem | 1st | 88.3 | 68.2 | 57.8 | 56.7 | 52.0 |
| | Low chem | 2nd | 90.6 | 72.4 | 59.7 | 56.6 | 53.1 |
| | High chem | 2nd | 90.4 | 64.4 | 57.8 | 54.8 | 49.2 |
| Pressurised $P_1$ | $PP_1$ 95˚C 120 min | 1st | 90.1 | 76.4 | 66.9 | 65.3 | 58.6 |
| | $PP_1$ 105˚C 60 min | 1st | 89.1 | 73.4 | 70.9 | 66.5 | 59.2 |
| | $PP_1$ 105˚C 120 min | 1st | 90.4 | 76.2 | 67.2 | 66.1 | 60.4 |
| Carbonate | High chem, 25 % $Na_2CO_3$ | 2nd | 90.7 | 68.9 | 60.0 | 57.7 | 51.7 |
| | High chem, 32.5 % $Na_2CO_3$ | 2nd | 91.2 | 70.8 | 61.6 | 58.4 | 53.1 |
| | High chem, 40 % $Na_2CO_3$ | 2nd | 92.7 | 72.1 | 64.2 | 61.1 | 55.4 |
| Sugar addition | Low chem, Gluc | 2nd | 92.0 | 84.9 | 63.0 | 60.0 | 54.6 |
| | Low chem, Xyl | 2nd | 91.1 | 81.0 | 63.5 | 57.6 | 53.1 |
| | Med. chem, Gluc | 1st | 90.7 | 70.9 | 67.3 | | 53.6 |
| | Med. chem, Xyl | 1st | 91.7 | 70.9 | 64.2 | 58.6 | 51.7 |
| | High chem, Gluc | 1st | 91.9 | 66.9 | 59.9 | 57.3 | |
| | High chem, Xyl | 1st | 92.0 | 71.2 | 59.1 | 56.4 | 50.1 |

## Alkali Substitution with $Na_2CO_3$

One option to decrease NaOH consumption in peroxide bleaching is to substitute NaOH partially with $Na_2CO_3$. Figure 7 illustrates the brightness development of the bleachings with partial alkali substitution of NaOH with $Na_2CO_3$ and the corresponding reference. All these bleachings were conducted from the second batch of 07Straw. The highest brightness was achieved with the 25% $Na_2CO_3$ share, and it was equal to that of the reference pulp. Increasing the substitution to 40% the final brightness decreased only from 68% to 65% ISO. Sodium carbonate substitution increased the bleached yield slightly, but it may also impair the defibration if the degree of substitution is 40% or above (Table 6).

The paper technical properties of the carbonate bleaching pulps were quite close to the reference pulp (Table 5). The substitution of sodium hydroxide with sodium carbonate in the bleaching decreased the Schopper Riegler number and increased the bulk of the bleached pulp compared to the reference pulp. Strength properties, such as tensile and tear index, were also lower than those of the reference pulp. This together with a higher yield of the pulp indicated that the use of sodium carbonate as an alkali source may impair the bonding of the pulps.

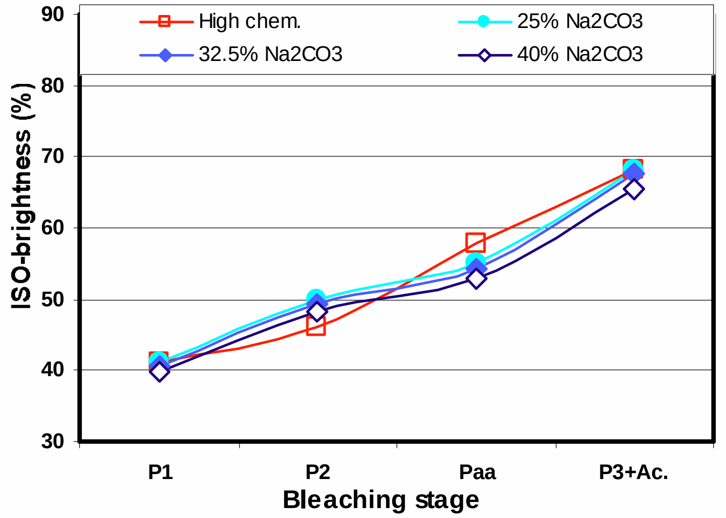

**Fig. 7.** Brightness of sodium carbonate substitution bleachings and reference pulp after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching.

## Sugar Addition

Particularly in the first alkaline peroxide stage, quite a lot of sugars dissolved because of the high alkali charge in that stage. The role of these sugars, especially glucose and xylose, was studied by adding them in the $P_1$ stage. The purpose of adding these sugars to the $P_1$ stage was to test the assumption of their negative effect on bleachability. However, glucose addition in the $P_1$ stage actually improved the pulp bleachability, since the final ISO brightness was 2 to 5% units higher than that of the reference pulp (Fig. 8). Xylose addition arrived at the same final brightness as the reference pulp. The negative effect was not to be seen. This may result from the reducing sugars' possible catalyst role in alkaline peroxide bleaching (Heikkilä and Vuorinen 2000; Vuorinen and Heikkilä 2003). The yield of sugar-addition bleaching trials was on a similar level to the yield of the comparable reference pulps (Table 6).

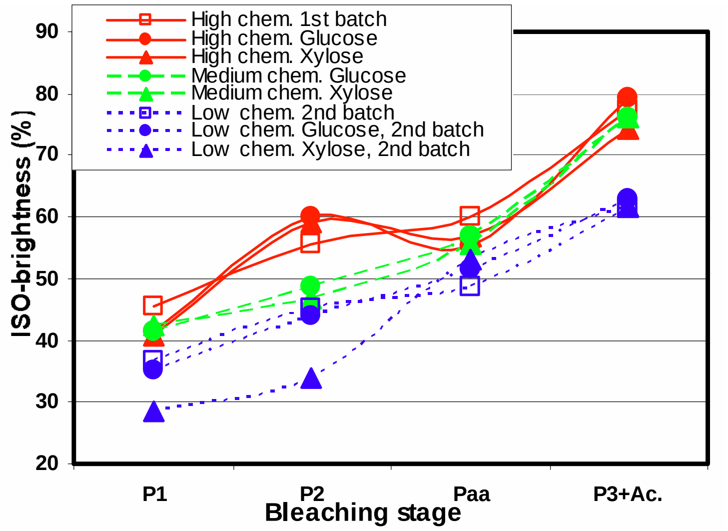

**Fig. 8.** Brightness of sugar addition bleachings and reference pulp after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching.

Table 5 presents the paper technical properties of the sugar addition pulps. Sugar addition did not have a significant effect on the paper technical properties. Xylose addition may impair the pulp drainability.

## Alkali Pretreatment

The alkali charge of the first peroxide stage was high, and organic substances were dissolved in abundance. These organic substances react further by consuming alkali. The idea of implementing an alkali pretreatment prior to the actual alkaline peroxide bleaching was to reduce sodium hydroxide consumption as much as possible in the following P stages while still being able to produce suitable fibres for paper making. The total NaOH consumption can be reduced from a level of 9 – 11.5% to 6 – 7%. The effect of such a reduction was a clearly lower final ISO brightness (15 to 24% units) and a higher yield (1.2-11.1% units) compared to the reference pulp. However, the alkali charge was not sufficient to defibrate the straw as well as in the case of the reference pulp. If a moderate mechanical treatment was to be combined with this bleaching and the brightness was not the main issue, then a pulp with acceptable properties could be achieved.

Figure 9 presents the ISO brightness and Fig. 10 presents the yield of the alkali-pretreated pulps and the reference as a function of NaOH consumption. The raw material of all alkali pretreatment bleachings was from the second batch of 07Straw, which was stored for two years in an unheated barn. The best response was probably achieved with atmospheric alkali pretreatment followed by the bleaching with sufficient alkali charge of about 5% NaOH on the original straw. The pressure in the alkali pretreatment did not significantly improve the final brightness of the pulp.

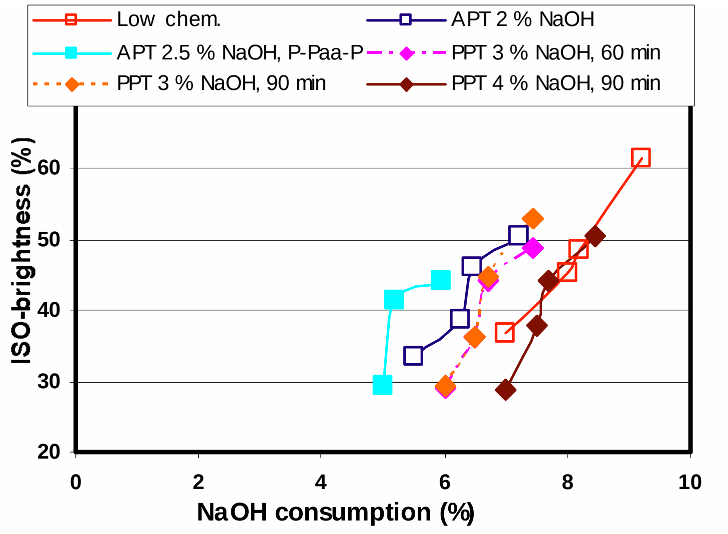

**Fig. 9.** Brightness of alkali pretreatment bleachings and reference pulp as a function of NaOH consumption. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by APT/PPT-P-P-Paa-P bleaching. APT alkali pretreatment, PPT pressurised alkali pretreatment.

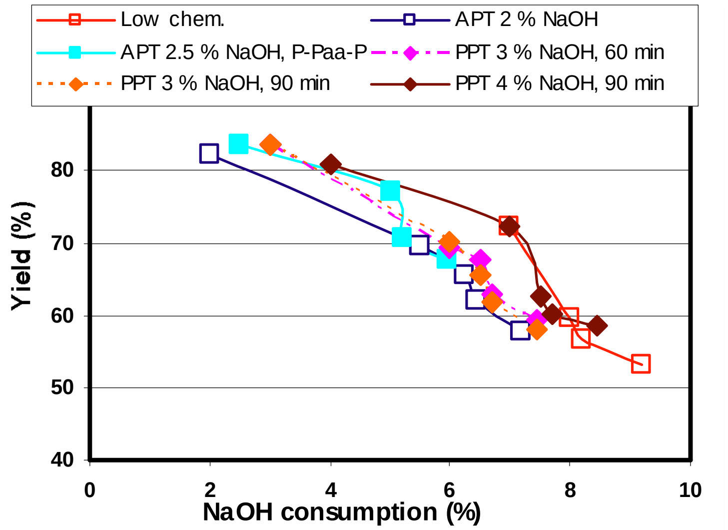

**Fig. 10.** Yield of alkali pretreatment bleachings and reference pulp as a function of NaOH consumption. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by APT/PPT-P-P-Paa-P bleaching. APT alkali pretreatment, PPT pressurised alkali pretreatment.

The reduction of sodium hydroxide consumption by an alkali pretreatment stage did not impair the pulp properties significantly, even though the yield of these pulps was higher and the bondability and thus the tensile index lower (Table 5). The short bleaching sequence P-Paa-P was not long enough to defibrate the pulp properly, and this may result in poorer pulp properties.

## CONCLUSIONS

1. The minimization of sodium hydroxide consumption in the peroxide bleaching of the hot water treated wheat straw is challenging. Straws grown during different years have a different chemical composition, and therefore, the amount of chemicals required in bleaching varies. The 2006 straw (06Straw) required less chemical to be bleached to 75% ISO brightness than the 2007 straw (07Straw).
2. Replacing NaOH with $Na_2CO_3$ is possible with a 25 to 40% share of total alkali. If the $Na_2CO_3$ share is 25%, the pulp properties are similar to the reference pulp properties. With higher sodium carbonate shares, the brightness is slightly lower than that of the reference pulp brightness.
3. It is possible to reduce the total alkali consumption of the alkaline peroxide bleaching of hot water treated straw by about 40% if an alkaline pretreatment stage is implemented prior to bleaching. This of course means also a clear reduction of 15 to 20% units in the final brightness, but the pulp properties are still acceptable. Therefore an alkali pretreatment and peroxide bleaching combined with a moderate mechanical treatment could be an acceptable possibility to minimise chemical consumption if the reduction of brightness is acceptable.
4. Sugar addition in the $P_1$ stage had an interesting influence on brightness. Glucose addition to the first peroxide stage delivered a higher brightness than that of the reference pulp. The reason for this may be that the reducing sugars act as catalysts in alkaline peroxide bleaching.
5. The oxygen pressure in the $P_1$ stage did not give a clear advantage compared to the unpressurised bleaching.
6. The most prevalent findings of this study indicate that the quality of pulp produced from wheat straw, when processed through the hot water treatment, and alkaline peroxide bleaching is satisfactory. If, however, the final application requires a high brightness level, this type of pulp may not be the most suitable one, due to the required amount of chemicals to attain such high brightness levels. Despite this disadvantage, wheat straw pulps have several applications, such as writing and printing papers, and packaging materials, where it can be regarded as the pulp of choice.

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Paper IV

# Storage of chemically pretreated wheat straw – A means to ensure quality raw material for pulp preparation

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# STORAGE OF CHEMICALLY PRETREATED WHEAT STRAW – A MEANS TO ENSURE QUALITY RAW MATERIAL FOR PULP PREPARATION

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The aim of this study was to evaluate effects of chemical pretreatment and storage on non-wood pulping and on pulp quality. The processes studied were hot water treatment followed by alkaline peroxide bleaching or soda cooking. The results showed that it is possible to store wheat straw outside for at least one year without significant changes in the raw material chemical composition and without adverse effects on the resulting pulp quality. The results are significant to the industry using non-woods to ensure the availability and the quality of the raw-material throughout the year in spite of the short harvesting time.

*Keywords: Chemical pretreatment; Storage; Wheat straw; Hot water treatment; Soda cooking*

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## INTRODUCTION

Most plants grown on farms yield considerable amounts of fibrous by-products (straw or stalk) that are not consumed by people. Only a minor proportion of the fibrous products is consumed by animals. In Finland, straw is usually chopped and mulched into soil, and a minute quantity is baled for bedding or animal feed.

Conserved forage has long been a major roughage feed for ruminants, helping them to remain productive during the winter period. In Finland about 70% of the grassland area is used for silage making (Tike 2009), nowadays most for wilted silage. In silage, different grass species are preserved under anaerobic conditions at the growth stage when they possess high amounts of water soluble carbohydrates and protein (McDonald et al. 1991). To prevent disadvantageous microbial functions and fermentation, the pH is usually decreased to level 4 by using organic acids such as formic acid, earlier even mineral acids (Virtanen 1933), which are mixed into grass or cereals during the silage making (McDonald et al. 1991). For straw, caustic soda (sodium hydroxide), ammonia, and urea treatments have long been used to improve the quality of material as animal feed (Wilkinson 1984; Sundstøl and Coxworth 1984).

The use of straw for non-food production (fibre, energy, bio-composites) has been the focus of many studies (Ilvessalo-Pfäffli 1995; Papatheofanous et al. 1996; Saijonkari-Pahkala 2001; Le Digabel and Avérous 2006; Coppola et al. 2009). The main problems associated with using non-wood materials industrially are the logistics of the bulky raw material and the usually short harvesting time. Hence, the non-wood raw materials usually are stored before industrial use. If the raw material is stored outside under prevailing climate conditions, moisture and biological activity can easily cause decay of the non-wood material. Known silage methods and farming machinery could possibly be used for storing the non-wood materials for industrial use. In short, the biomass can be stored in bales without a need for extra storehouses.

The aim of this study was to evaluate the effects of chemical pretreatment and storage on wheat straw pulping and on pulp quality. The processes studied were hot water treatment followed by peroxide bleaching or soda cooking.

## EXPERIMENTAL

### Raw Material

Spring wheat straw harvested in 2007 (07Straw) and 2008 (08Straw) was used in the experiments. The wheat varieties were Marble in 2007 and Kruunu in 2008. The growing site for wheat was on a sandy clay field in Jokioinen, Finland (60°49'12"N, 23°28'12"E). The 07Straw was collected after threshing and cut into pieces with a laboratory cutter. The 08Straw was baled with a chopper baler, and treated with formic acid based solution one day after threshing, the targeted amount was 9 mL/kg of fresh straw. The distance between baler's knives were 8.6 cm, and the resulting straw length was 4-10 cm. Additionally, some 08Straw was collected after threshing and cut into pieces with the laboratory cutter for the minisilo experiments.

### Chemical Pretreatment/Storage in Plexiglass® Acrylic Silos

Urea or formic acid was used as pretreatment/storing chemicals in Plexiglass® acrylic silo trials. The formic acid charge was 15g/kg DM, and the concentration of the used solution was 85%. The urea charge was 44g/kg DM, and the concentration of the used urea solution was 40%. The dry content of the chopped 07Straw was 74.4%. Straw and chemical were mixed carefully before weighing the mixture into the silos. The straw amount weighed was 900 g, including the weight of added acid or urea. The straw was packed with a wooden "piston" into the silos. The density of packed straw in silos was approximately 127 kg DM/m$^3$. Figure 1 presents the Plexiglas® acrylic silos used for the chemical pretreatment. In selected testpoints two replicates were performed.

The time of storage was varied from about 2 months to 1 year. After the period of storage, the silos were opened and the straw was washed. First, about 450 g of the straw was diluted with 10 L of deionised water, agitated, and left to settle for 30 min. Then the straw was centrifuged and washed with 20 L of deionised water while still centrifuging. The washed straw was stored in a cold storage room (+5°C) before the following experiments.

The untreated straw is not preserved at the room or cold storage temperature, if it is not air dried before storing. The straw with dry matter content of about 75% will become moulded quite rapidly in an air-proof plastic tube. Therefore, the reference points for untreated straw were excluded due to their possible health risks to the researchers and regarding the scientific value of such trials.

**Fig. 1.** Storage of chemically pretreated wheat straw in Plexiglass® acrylic silos. Sealing with Plexiglass® plate, lead weight, and water seal.

## Chemical Pretreatment/Storage in Round Bales

Formic acid based solution AIV 2 Plus preservative from Kemira Oyj (76% formic acid, 5.5% ammoniumformate, water) was used as a pretreatment/storing chemical in the round bale trials. The straw was baled with the chopper baler and the acid was applied at the rate 9 mL/ kg of fresh straw during baling using a pump applicator attached to the baler. The density of straw in round bales was 107 kg/m$^3$. The dry matter content of the fresh 08Straw was 85.4%. After the baling, the straw was wrapped with 10 layers of white RaniWrap® stretch film (low-density polyethylene, width 750 mm, thickness 0.025 mm, Ab Rani Plast Oy, Finland) with 50% overlapping and 70% pre-streching.

**Fig. 2.** Storage of chemically pretreated wheat straw in round bales. Wrapping of the bale with white stretch film.

The raw material used for the experiments was taken after storing the bales 27, 41, and 52 weeks in an unheated barn. During the time the temperature of single days varied from -21 to +29°C according to the Finnish Meteorological Institute, and the mean temperatures are given in Table 1. After the defined time the bale was opened and the straw sample was collected evenly from the whole bale. The sample was frozen directly without washing for further use. Figure 2 illustrates the wrapping of the round bales used for chemical pretreatment.

**Table 1.** Weather Conditions in Jokioinen, Finland during the Round Bale Trials. Means for Daily Temperatures (Mean, Minimum and Maximum, °C) Given Monthly from October 2008 to September 2009, Jokioinen, Finnish Meteorological Institute. Baling Day 2008-09-24. Sampling Days 2009-04-03, 2009-07-07 and 2009-09-24 (Year-Mm-Dd).

| Year/Month | Mean Temp. °C | Min. Temp. °C | Max. Temp. °C |
|---|---|---|---|
| 2008/10 | 7 | 4 | 10 |
| 2008/11 | 1 | -1 | 4 |
| 2008/12 | 0 | -2 | 1 |
| 2009/01 | -5 | -8 | -2 |
| 2009/02 | -5 | -9 | -3 |
| 2009/03 | -3 | -6 | 1 |
| 2009/04 | 4 | -1 | 10 |
| 2009/05 | 11 | 5 | 17 |
| 2009/06 | 13 | 8 | 19 |
| 2009/07 | 16 | 11 | 22 |
| 2009/08 | 15 | 10 | 21 |
| 2009/09 | 12 | 8 | 17 |

*Temperature Sum 2073°C (base 0°C)*

### Chemical Pretreatment/Storage in Minisilos (glass bottles)

Formic acid or formic acid based preservative was used as a pretreatment/storing chemical in the minisilo trials. The amount of the formic acid solution (85% solution) added was the same as in the Plexiglass® acrylic silo experiment, which was 15g/kg DM acid. The formic acid based preservative charge was about the same as in the round bale experiments, 9 mL/ kg of fresh straw. The dry content of the chopped 08Straw was 85.4%. The dry content of the straw in silos was adjusted with mixture of water and preservative solution to 75%. The chemical and water were carefully mixed with the straw. Then the straw amount (32 g) was weighed into each minisilos, including the weight of water and added acid. The straw was pressed with a plastic "piston" while adding it into the silos. The density of packed straw in minisilos was 200 kg/m$^3$, which was higher than that of round bales or Plexiglass® Acrylic Silo experiments. This was most likely due to the slightly shorter length of the straw pieces. The storing time varied from 1 month to 1 year. Figure 3 presents the sealing of minisilos used for the chemical pretreatment.

After the defined time the silo was opened and the straw was washed. The washing started with dilution of straw with 3 L deionised water, agitation, and settling for 20 minutes. After that the straw was thickened and washed twice by diluting it with 3 L deionised water and thickening. After the last washing the straw was centrifuged and air-dried and, finally, the air dry straw was frozen in polyethylene bags. The straw from the minisilo pretreatment was used for the chemical composition analysis.

**Fig. 3.** Chemical storing of wheat straw in minisilos. Sealing with gray rubber plug and white plastic cap.

## Hot Water Treatment and Bleaching

The pretreated straw was treated with hot water using an air-heated digester equipped with six 2.5 L autoclaves as described earlier (Leponiemi et al. 2010). The treatment temperature was 120°C, and the time at temperature 60 min. Diethylene triamine pentaacetic acid (DTPA) charge in treatment was 0.2%. The bleaching sequence was based on alkaline peroxide (P) and peracetic acid (Paa): P-P-Paa-P. The procedure was also described earlier (Leponiemi et al. 2010). Bleaching conditions are shown in Table 2. After the hot water treatment and every bleaching stage the treated straw/pulp was washed. Washing was carried out by diluting the treated straw or pulp with deionised water, agitating, allowing it to settle for 2 minutes and by removing the excess water through a wire pouch. The dilution and thickening were repeated 3 times. After the last washing the straw was centrifuged to 25% consistency. After the last bleaching stage and washing, the pulp was acidified. The pulp was diluted with deionised water and dilute sulphuric acid was added, until the pH reached roughly 3.8. After 15 minutes, the final pH was between 4 and 4.5. After the acidification the pulp was washed again, as explained before. The selected testpoints were repeated to evaluate the repeatability of the trials.

## Soda Cooking

The soda cooking was performed with the same air-heated digester as the hot water treatment. The cooking temperature was 160°C, and the time at cooking temperature was 60 min. The temperature was raised to 80°C within 30 min, and after that to the selected cooking temperature at a rate of 1°C/min. Liquor to straw ratio was 5 and the effective alkali varied from 12 to 16% on the straw. After soda cooking, the pulp was washed as described earlier.

**Table 2.** Bleaching Conditions of Hot Water Treated Straw with a P-P-Paa-P Bleaching Sequence. *

| Raw material | Straw from Plexiglass acrylic silos | Straw from round bales |
|---|---|---|
| **P1 stage** | | |
| Temperature, °C | 85 | 85 |
| Time, min | 180 | 180 |
| Consistency, % | 9-10** | 10 |
| NaOH charge, % on straw | 8.5 | 7.0 |
| $H_2O_2$ charge, % on straw | 5.0 | 4.0 |
| **P2 stage** | | |
| Temperature °C | 85 | 85 |
| Time, min | 180 | 180 |
| Consistency, % | 7-10** | 10 |
| NaOH charge, % on straw | 2.0 | 1.0 |
| $H_2O_2$ charge, % on straw | 2.0 | 2.0 |
| **Paa stage** | | |
| Temperature, °C | 85 | 85 |
| Time, min | 60 | 60 |
| Consistency, % | 6-10** | 10 |
| NaOH charge, % on straw | 0.2 | 0.2 |
| Paa charge, % on straw | 1.0 | 1.0 |
| **P3 stage** | | |
| Temperature, °C | 85 | 85 |
| Time, min | 180 | 180 |
| Consistency, % | 5.5-10** | 10 |
| NaOH charge, % on straw | 1.5 | 1.0 |
| $H_2O_2$ charge, % on straw | 2.0 | 2.0 |

* P = Alkaline peroxide stage; Paa = Peracetic Acid Stage.

** Bleaching yield was not noted in all test points, the bleaching consistency lower in these testpoints.

## Analyses

Paper technical properties of hot water treated and peroxide-bleached wheat straw pulps were analyzed according to SCAN test methods. The kappa number of soda cooked wheat straw pulp was also analyzed according to the SCAN test method.

The carbohydrates and lignin composition were analysed according to the NREL/TP-510-42618 method (Sluiter et al. 2008). The monosaccharides were determined after acid hydrolysis treatment with high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD analysis). A Dionex ICS-3000 liquid chromatography and the anion-exchange column CarboPac PA20 were used for analysis. A minimum of two parallel runs with HPAEC were performed. The extractives were analyzed according to the SCAN-CM 49:93 test method.

Ash and multi-element determination of untreated straw samples started with drying the samples at 105°C and grinding the samples in a hammer mill. For multi-element analysis the samples were then ground again in a Fritsch Pulverisette grinder and dried at 105°C. Samples were ashed at 550°C for 12 hours before hydrogen fluoride-nitric acid dissolution. These solutions were analyzed with the inductively coupled plasma mass spectroscopy (ICP-MS) technique for multi-element contents. The ash content of the pretreated straw samples was analysed according to the SCAN-C6:62 test method (525°C, 4 hours).

## RESULTS AND DISCUSSION

### Chemical Pretreatment of the Straw with Urea or Formic Acid

The straw from the plexiglass acrylic silo treatments with urea or formic acid was washed after the pretreatment, and the pretreatment yield was estimated from the dry content of the washed straw. The yield of urea-treated straws was 91% independent of the treatment time, and the yield of formic acid treated straws was 93%, respectively. The washing yield of untreated straw was 97%; therefore, about 3% units of the yield loss in pretreatment can be explained by the loss of fines during washing.

The urea pretreatment darkened the straw due to the alkali darkening, but the formic acid pretreatment did not have an effect on the straw colour. The pH measured from the first washing filtrate remained approximately constant, regardless of pretreatment time, 8.9 for urea pretreatment and 6.7 for formic acid pretreatment. Urea is converted by bacteria on straw to ammonia, which then acts to process the straw as an alkali. The chemical treatment with alkalis softens the lignin structure (Butterworth 1985) and may modify the lignin-carbohydrate complex in straws, making the cellulose and hemicelluloses fractions more accessible. A chemical treatment with acid could be even more effective (Butterworth 1985).

Formic acid has an antibacterial effect due both to hydrogen ion concentration and to a selective bactericidal action of the undissociated acid. Formic acid lowers the pH and thus limits fermentation and reduces the degradation of proteins to ammonia. The effect of formic acid application on the chemical composition of silage varies according to the level applied, the dry matter content of the ensiled material, and the species of crop (McDonald et al. 1991). When the dry matter content is higher, the effects of the preservative are lower. The changes in the chemical composition of the raw material are therefore assumed to be limited in the studied dry matter when the dry content is greater than 70%.

After about half a year of storage of the pretreated straw the bottom and top parts of the silos were slightly mouldy. This was probably due to some air leaking through the sealings or the air left inside the straw centre. The straws from the centre part of the silo were used in the experiments, and therefore the mould probably did not affect the results.

## Chemical Composition of the Pretreated Straws with Formic Acid or Formic Acid Based Preservative

The chemical pretreatment with formic acid or formic acid based preservative did not change the chemical composition of wheat straws significantly. Table 3 presents the chemical composition of the wheat straw used in the minisilo experiments and the chemical composition of the treated straws. The sugar results from separate HPAEC runs were very close to each other, the sample preparation, however, caused slight variation. Due to the preliminary nature of the findings, the need for statistically planned follow-up work is stated. Nevertheless the variation of the results in Table 3 is minute, and therefore it can be assumed that the chemical pretreatment with formic acid or formic acid based preservative does not significantly affect the chemical composition of wheat straw.

The total amount of sugars and gravimetric lignin seemed to be higher in the treated straws compared to the untreated straw. This higher organics content of the treated straws may be due to the dissolution/losses of ash and fines during the pretreatment or the following washing stage. The chemical pretreatment with formic acid or formic acid based preservative may also loosen the straw structure and thus enhance the acid hydrolysis in the chemical composition analysis. The formic acid treatment resulted in a lower pH of the washing filtrate compared to the treatment with formic acid based preservative and thus lower ash content of the treated straws. Morrison showed that formic acid silage (Morrison 1979) decreased hemicelluloses content of ryegrass 10-20% but did not affect the amounts of lignin or cellulose. In the case of lucerne silage (Morrison 1988) the formic acid decreased the cellulose content but had less effect on the hemicelluloses fraction. He explained the results by the differences in the grass structures. The dry content of these wilted silages was not mentioned but it most probably was much lower than that of the straw silages performed in the present experiments.

The chemical pretreatment of the straws was performed at a fairly high dry matter content (75%); therefore the changes in the chemical composition were expected to be somewhat limited. The chemical composition of the round bale treatments with formic acid based preservative are presented in Table 4. The results are in line with those from the minisilo experiments. The variation of the results may be due to the heterogeneity of the straws in different bales, and also the charge of formic acid based preservative may have slightly varied within the bales.

The bales treated with formic acid based preservative where not observed to be moulded by organoleptic evaluation. This is an important factor in regard to occupational health of the raw-material handlers and their exposure to fungal particles. The reference bale without chemical pretreatment was slightly mouldy after one year storage in an unheated barn. The bale expelled an excessive amount of small particles in the air during opening and also a mildewy smell was observed, despite of the high dry matter content and the shelter from the weather. However, the slight mould growth did not significantly affect the chemical composition of the straw compared to the corresponding frozen sample. On the other hand, the outdoor storage in the field has been reported to have significant effects on the chemical composition of straw. Bicho and McRae (2004) exposed Canadian wheat straw to the wheather for one year and discovered evidence of decay throughout the bales.

**Table 3.** Chemical Composition of Wheat Straw and Treated Wheat Straw. Results from Minisilo Experiments

| Sample | 08Straw | 08 Straw Formic acid | | | | 08Straw Formic acid based preservative | | | |
|---|---|---|---|---|---|---|---|---|---|
| Pretreatment time, months | frozen | 3 | 6 | 9 | 12 | 3 | 6 | 9 | 12 |
| Carbohydrates, mg/100 mg | | | | | | | | | |
| Glucan | 37.9 | 43.8 | 43.2 | 42.7 | 42.9 | 43.6 | 43.5 | 42.3 | 42.7 |
| Xylan | 18.6 | 22.2 | 21.6 | 21.5 | 21.7 | 21.1 | 21.1 | 20.7 | 21.3 |
| Arabinan | 2.1 | 2.5 | 2.3 | 2.4 | 2.4 | 2.6 | 2.5 | 2.5 | 2.5 |
| Galactan | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| Mannan | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| Rhamnan* | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL | <DL |
| Total | 59.8 | 69.8 | 68.3 | 67.8 | 68.1 | 68.6 | 68.3 | 66.6 | 67.7 |
| Lignin, % | | | | | | | | | |
| Gravimetric lignin (ash inc.) | 23.0 | 23.4 | 23.8 | 25.0 | 25.3 | 24.5 | 25.0 | 24.0 | 24.2 |
| Gravimetric lignin (ash exc.) | 18.9 | 19.7 | 18.8 | 20.9 | 20.9 | 19.4 | 19.6 | 19.1 | 19.2 |
| Soluble lignin | 3.2 | 1.9 | 1.9 | 1.8 | 1.9 | 2.1 | 2.1 | 2.1 | 2.2 |
| Acetone extractives, % | 1.72 | 1.65 | 1.65 | 1.67 | 1.74 | 1.56 | 1.62 | 1.87 | 1.77 |
| Ash, % | 8.6 | 6.2 | 6.4 | 6.8 | 7.5 | 8.2 | 7.9 | 7.2 | 7.6 |
| Metals, mg/kg straw | | | | | | | | | |
| Silica | 36451 | | | | | | | | |
| Magnesium | 875 | | | | | | | | |
| Calcium | 2291 | | | | | | | | |
| Potassium | 14157 | | | | | | | | |
| Iron | 97.8 | | | | | | | | |
| Manganese | 12.2 | | | | | | | | |
| Copper | 4.59 | | | | | | | | |
| Total (lignin, polysaccharides, extractives, ash), % | 92.2 | 99.3 | 97.1 | 98.9 | 100.2 | 99.8 | 99.5 | 96.9 | 98.4 |

* <DL = under detection limit 0.1 mg/100mg

The decay caused losses in the galactan, arabinan, and ash contents, while the xylan level remained constant and lignin and glucan contents increased. These results concur with those of Collins et al. (1990), which indicate that water soluble components, such as ash and some water soluble polysaccharides, are rapidly leached from exposed straw.

## Hot Water Treatment and following Peroxide Bleaching of the Pretreated Straws

The yield loss of chemical pretreatment with urea or formic acid was practically compensated in hot water treatment. The yield of hot water treatment was 95% for urea-treated straw (i.e. 86% of original straw) and 96% for formic acid-treated straw (i.e. 89% of original straw) compared to 88% of untreated straw. The bleached yield was also almost the same for pretreated and reference pulp.

The brightness of hot-water-treated and bleached pulp was affected by the pretreatment chemical and time. After 2-6 months of pretreatment time, the pulp brightness was clearly lower, as can be seen in Fig. 4. The decline in brightness in the case of formic acid treatment may be due to the lignin structure alteration caused by the acid addition (Leschinsky et al. 2008; Shiming and Lundquist 2000).

**Table 4.** Chemical Composition of Wheat Straw and Pretreated Wheat Straw. Results from Round Bale Experiments

| Sample | 08Straw frozen | 08Straw outside (ref.bale) | 08Straw Formic acid based preservative outside (round bales) | | |
|---|---|---|---|---|---|
| Pretreatment time, months | - | 12 | 6.3 | 9.4 | 12.0 |
| Carbohydrates, mg/100 mg | | | | | |
| Glucan | 37.9 | 40.8 | 43.1 | 41.0 | 43.9 |
| Xylan | 18.6 | 20.5 | 21.7 | 20.9 | 23.1 |
| Arabinan | 2.1 | 2.4 | 2.4 | 2.5 | 2.5 |
| Galactan | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| Mannan | 0.5 | 0.5 | 0.4 | 0.3 | 0.5 |
| Rhamnan* | <DL | <DL | <DL | <DL | <DL |
| Total | 59.8 | 65.0 | 68.3 | 65.6 | 70.8 |
| Lignin, % | | | | | |
| Gravimetric lignin (ash inc.) | 23.0 | 23.3 | 24.3 | 24.4 | 23.8 |
| Gravimetric lignin (ash exc.) | 18.9 | 18.9 | 19.2 | 19.5 | 19.1 |
| Soluble lignin | 3.2 | 2.3 | 2.2 | 2.1 | 2.1 |
| Acetone extractives, % | 1.72 | 1.67 | 1.70 | 1.68 | 1.75 |
| Ash, % | 8.6 | 8.9 | 7.7 | 8.4 | 7.7 |
| Metals, mg/kg straw | | | | | |
| Silica | 36451 | | | | |
| Magnesium | 875 | | | | |
| Calcium | 2291 | | | | |
| Kalium | 14157 | | | | |
| Iron | 97.8 | | | | |
| Manganese | 12.2 | | | | |
| Copper | 4.59 | | | | |
| Total (lignin, polysaccharides, extractives, ash), % | 92.2 | 96.8 | 99.1 | 97.3 | 101.5 |

* <DL = under detection limit 0.1 mg/100mg

Urea pretreatment reduced the brightness of hot water treated and peroxide bleached pulp even more. The colour difference was already visible in the pretreated straws. The darkening in the pretreated straws derives from the alkali darkening. The urea is converted to ammonia during the pretreatment, which then forms ammonium with water. The balance of ammonia and ammonium ions is transferred to ammonia when hydroxide ions are added in an alkaline peroxide stage. A part of the added hydroxide is consumed in this side reaction instead of the actual bleaching reaction, thus impairing the bleachability.

After about 9 months of storage, the situation changed. The bleachability of pretreated straw with both formic acid and urea was clearly improved. The better bleachability may be due to the loosened structure of wheat straw or lignin alteration. Furthermore the dissolution of sugars during the pretreatment or the hot water treatment may have a positive effect on the bleachability. Mustajoki et al. (2010) reported that the addition of glucose or xylose to the first peroxide stage of a P-P-Paa-P bleaching sequence for hot water treated wheat straw improved the pulp bleachability.

The results of straws treated with formic acid based preservative from round bale experiments showed a similar trend in the final brightness of hot water treated and peroxide bleached wheat straw pulp (Fig. 5). First the brightness decreased, but turned to increase after the above 9 months pretreatment time. The change appears after longer pretreatment time compared to the Plexiglass acrylic silo treatments. This may be due to the storage temperature: the round bales were stored in an unheated barn where the temperature was clearly lower compared to the silo experiments at room temperature.

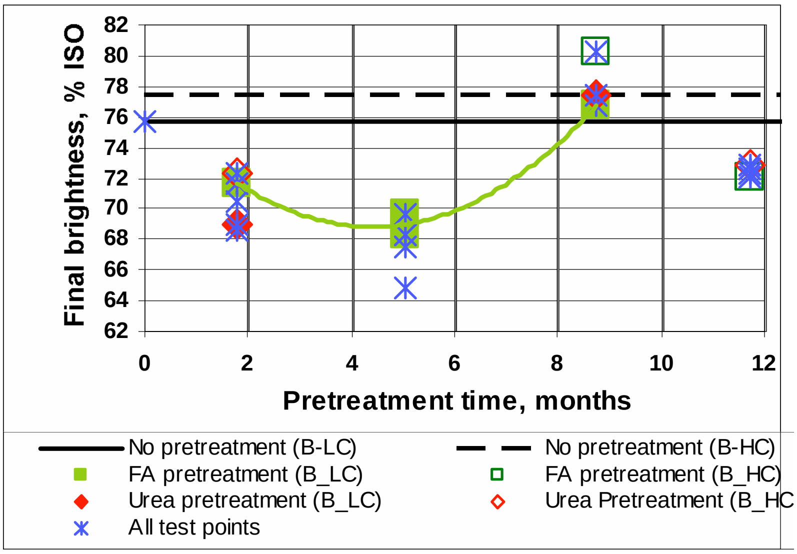

**Fig. 4.** Final brightness as a function of straw pretreatment time. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. P = alkaline peroxide stage, Paa = peracetic acid stage. Pretreatment in Plexiglas acrylic silos. FA = Formic cid. B-LC = lower bleaching consistency (<10%), B-HC = higher bleaching consistency (10%).

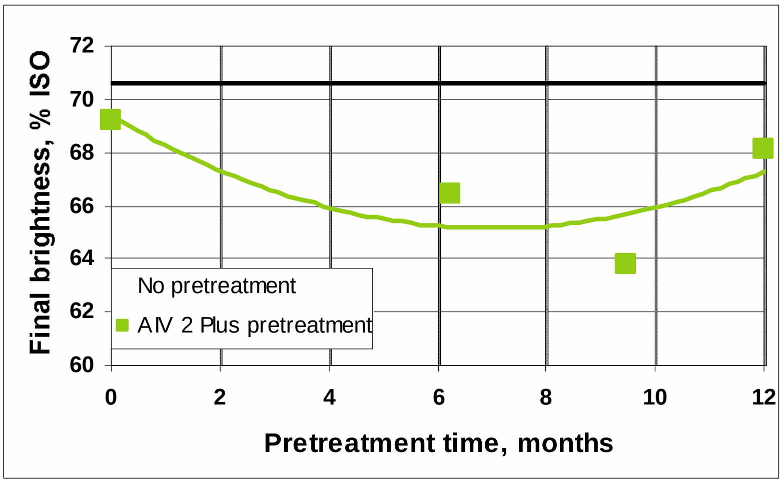

**Fig. 5.** Final brightness as a function of straw pretreatment time. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. Pretreatment in round bales.

The chemical pretreatment did not affect the paper technical properties significantly, as is evident in Table 5 (see Appendix). Bicho and McRae (2004) reported that the field storage of Canadian wheat straw decreased pulp freeness and tear strength. In these studies, the straw bales were also frozen over the winter months and thus were less susceptible to weathering. In milder climates, moisture and heat may have a much higher impact on the paper technical properties of the produced pulp.

## Soda Cooking

It is possible to combine a chemical pretreatment / storing stage also with a soda cooking process, especially if the pretreatment is performed with formic acid (Fig. 6). Urea treatment has a negative effect on the delignification due to the consumption of hydroxide ions in the side reaction of ammonium and hydroxide to ammonia. This observation suggests that the storage of straw with sodium hydroxide could be one possibility to ensure high-quality raw material to soda pulp mills and even reduce the cooking chemical consumption.

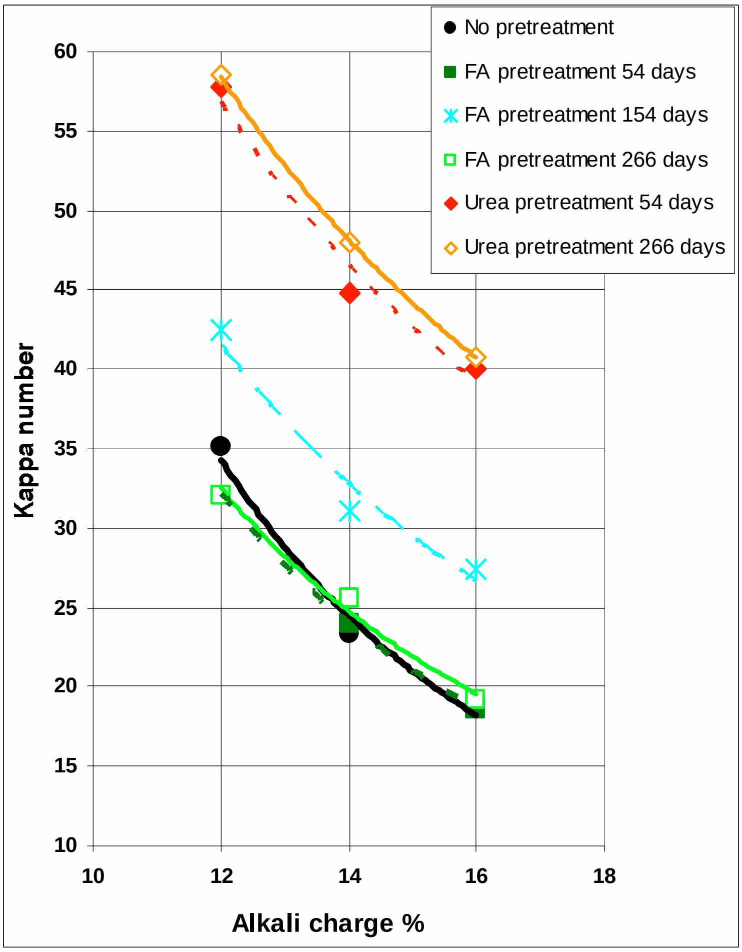

**Fig. 6.** Kappa number as a function of straw pretreatment time. Soda cooking at 160°C for 60 min. Pretreatment in Plexiglas® acrylic silos.

## CONCLUSIONS

1. It is possible to integrate the chemical pretreatment stage / storing of straw or other non-woods with an existing pulping process. The chemical storing ensures more homogenous raw material resources throughout the year to mills that utilize non-wood materials. Furthermore, no large storing houses are required; hence the straws can be stored on farms with existing equipment.
2. The storage of chemically pretreated straw could also be integrated with energy processes or other processes that utilize non-woods as a raw-material. The uniform raw material is a relevant issue to these mills as well.
3. Formic acid is a potential preservative, but formic acid based preservative could also be used as a preservative if it is otherwise available on the farms.
4. Urea is not such a desired storing chemical, as it increases the sodium hydroxide consumption in the following process. This manifests itself as decreased pulp bleachability of hot water treated straw or as an increased kappa number of soda cooked pulp.
5. Due to the preliminary nature of this study, the chemical charges in the pretreatment are to be systematically optimised and their effects evaluated in further studies. The use of other possible chemicals, such as sodium hydroxide should also be investigated.
6. The storage of pretreated straw did not significantly affect the chemical composition of the straws or the paper technical properties of the produced pulps. If the storage time is very short, and the straws can be protected from the weather, the chemical process may not be the most advantageous option.

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## APPENDIX

**Table 5.** Paper Technical Properties of Hot Water Treated and Peroxide Bleached Pulps. Pretreatment with Urea, Formic (Plexiglass Acrylic Silo Experiments) or Formic Acid Based Preservative (Round Bale Experiments).

| Pretreatment chemical | 07Straw Ref. | 07Straw Urea (room temp.) | | | 07Straw Formic acid (room temp.) | | | | 08Straw Ref. | 08Straw Formic acid based preservative (outside) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pretreatment time, months | 0 | 8.7 | 11.7* | 11.7* | 5.1 | 8.7 | 8.7* | 11.7* | 0 | 6.3 | 9.4 | 12 |
| ISO brightness % | 75.7 | 77.4 | 77.3 | 77.0 | 69.0 | 76.7 | 80.3 | 74.8 | 70.6 | 66.4 | 63.8 | 68.1 |
| SR | 50 | 41 | 36 | 42 | 37 | 40 | 40 | 43 | 35 | 24 | 32 | 40 |
| Grammage, g/m$^2$ | 61.4 | 64.0 | 63.5 | 63.6 | 63.5 | 64.8 | 63.9 | 62.8 | 63.0 | 63.2 | 67.5 | 65.3 |
| Thickness, µm | 86 | 101 | 90 | 88 | 88 | 102 | 100 | 93 | 101 | 92 | 98 | 102 |
| Apparent density, kg/m$^3$ | 714 | 637 | 706 | 725 | 724 | 634 | 640 | 672 | 664 | 689 | 692 | 637 |
| Bulk, m$^3$/t | 1.40 | 1.57 | 1.42 | 1.38 | 1.38 | 1.58 | 1.56 | 1.49 | 1.51 | 1.45 | 1.45 | 1.57 |
| Opacity, % | 66.6 | | | | 70.0 | | | | | 67.5 | 67.8 | 70.4 |
| Light scattering coeff., m$^2$/kg | 21.5 | | | | 20.5 | | | | | 21.2 | 18.9 | 21.8 |
| Roughness, ml/min | 1800 | 2250 | 2036 | 2050 | 1771 | 2116 | 2128 | 2040 | 1796 | 2721 | 1662 | 2023 |
| Air permeance, ml/min | 35.0 | 32.0 | 25.6 | 24.2 | 25.3 | 32.0 | 32.0 | 25.2 | 66.2 | 70.2 | 27.4 | 29.4 |
| Tensile index Nm/g | 71.9 | 65.0 | 74.6 | 76.9 | 75.2 | 63.4 | 63.5 | 71.0 | 86.7 | 90.6 | 86.6 | 82.0 |
| Tensile stiffness index, MNm/kg | 7.5 | 6.7 | 6.8 | 7.4 | 7.3 | 7.1 | 6.6 | 6.7 | 6.9 | 6.3 | 6.5 | 7.3 |
| Stretch, % | 2.2 | 2.6 | 3.7 | 3.3 | 2.4 | 2.0 | 2.3 | 3.1 | 2.8 | 3.2 | 2.9 | 2.6 |
| Tensile energy, mJ/g | 1049 | 1150 | 1850 | 1798 | 1053 | 853 | 1002 | 1475 | 1298 | 1435 | 1283 | 1256 |
| Burst index, kPam$^2$/g | 3.9 | 4.4 | 5.1 | 5.2 | 3.8 | 4.7 | 4.8 | 6.1 | 5.7 | 4.3 | 4.3 | 4.4 |
| Tear index, Nm$^2$/kg | 3.9 | 3.8 | 3.7 | 3.8 | 3.8 | 4.3 | 4.5 | 4.2 | 4.3 | 4.1 | 4.0 | 4.1 |

*Higher consistency in bleaching

Paper V

# Assessment of combined straw pulp and energy production

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# ASSESSMENT OF COMBINED STRAW PULP AND ENERGY PRODUCTION

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The aim of this study was to evaluate the potential of a new, straw-based fibre manufacturing technology integrated to bioenergy and biofuels production. The process is based on a novel hot water treatment and subsequent mechanical refining, both of which are performed at a high temperature. Soda process, ethanol production, and chemical defibration based on hot water treatment and subsequent alkaline peroxide bleaching were selected as references. The idea is to utilise the fibre fraction for packaging and the dissolved solids and the formed fines for energy. The investment costs of this process are significantly lower than those of a soda process. Additionally, a chemicals recovery process is unnecessary. Furthermore, the process offers an attractive alternative for biogas production. However, the assessment showed that the process could only be economical in some terms. Subsidies for investment would probably be needed to promote the acceptance of this environmentally safe process.

*Keywords: Non-wood fibre; Wheat straw; Biorefinery; Hot water treatment; Mechanical refining; Assessment; Pulp; Energy*

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## INTRODUCTION

Non-wood pulping processes are typically chemical or chemi-mechanical processes (Leponiemi 2008). Up to now, very few results of pulp properties from non-wood based mechanical pulp without chemical impregnation have been reported. Extrusion pulping process is one of the rare processes that has been mentioned for the processing of non-woods such as bast fibres without chemicals (van Roekel et al. 1995). However, hemp bast fibres differ significantly from short fibre non-wood raw materials, such as wheat straw. The lignin content of bast fibres is significantly lower and the fibres are extremely long. The mechanical fibres are usually stiff, coarse and straight. In addition, fines are formed during refining. Therefore the strength properties of mechanical pulps are lower than those of chemical pulps.

The results of our previous research have shown that it is possible to produce pulp from wheat straw by a simple procedure based on a hot water treatment and subsequent mechanical defibration (Leponiemi et al. 2010). In this paper this process is referred to as the “mechanical” approach. The novelty of the process comes from the idea of utilising the reject material not suitable for pulp fibre, such as dissolved solids or fines, for energy production. The drainability of the produced pulp was good, but the strength properties were low (Leponiemi et al. 2010).

Wood-based mechanical pulping research indicates that by increasing the refining temperature, the energy consumption in refining is reduced and mechanical pulp properties are maintained or even improved, but the optical properties are reduced. (Muenster 2005; Nurminen 1999; Höglund et al. 1994, 1995; Sabourin et al. 1996). Therefore, it was thought worthwhile to investigate the possibility of improving the mechanical wheat straw pulp properties and reducing energy consumption in refining by the use of elevated temperature in hot water treatment and mechanical refining. The bonding properties of the fibres may be improved simultaneously.

A hydrothermal pretreatment of lignocellulosics is known to enhance both bioethanol and biogas production. Since such a treatment of straw material is similar in fibre and energy production, the aim of this work is to investigate the synergistic benefits of combining fibres and energy production from wheat straw. The assumption is that mechanical pulp with adequate quality for packaging can be produced by conventional refining equipment at high temperature, while the residue can be utilized for energy production.

The aim of this work was to determine the potential and estimate the cost level of the suggested process. Soda pulping, ethanol production and chemical pulping process, including hot water treatment and the subsequent alkaline peroxide bleaching (Leponiemi et al. 2010; Mustajoki et al. 2010) were selected as the references for the suggested process. In this paper the chemical pulping process is referred to as the "chemical" approach.

## EXPERIMENTAL

### Mechanical Refining Experiments at High Temperature

*Raw material*

Air-dried wheat straw was used as a raw material for the experiments. The straw was cultivated in Jokioinen, Finland and harvested during the summer of 2007. The straw was chopped at the end of the threshing machine, air dried, and stored in an unheated barn for about two years. The fines were removed by using a screen described in the standard SCAN-CM 40:88. The diameter of screen holes was 6 mm and the screening time was 30 s. The dry matter content of the screened straw was determined according to the standard SCAN-CM 39:88.

*Hot water treatment*

The hot water treatment was performed in 2.5 L autoclaves of an air-heated rotating digester. The hot water treatment temperature was 170 °C, the time 45 min, and the water to straw ratio 10:1. Deionised water was used, and no chemicals were added in the treatment.

The treated straw was then washed by diluting it with deionised water, agitating, leaving the mixture to settle for 2, minutes and removing the excess water through a wire pouch. Dilution and thickening were repeated 3 times. Finally, the washed straw was centrifuged to 25% consistency.

### *Mechanical refining*

The batch type wing defibrator at Aalto University, in the Department of Forest Products Technology, was used for the refining experiments at 170°C temperature. The refiner was first preheated with direct steam to 170°C. Then the hot water treated straw was placed in the lockers between the blades and the cover was closed. The refining was started by preheating the straw with direct steam for 5 min, during which the blades were rotated a couple of times manually to ensure even heating. After the heating, the motor of the defibrator was started. The amount of straw used in refining was 75 g abs. dry. The refining time was 2 to 4 s, the speed of rotation 60 r/min, and the distance between the stator and the rotor 1 mm. The very short refining time and the relatively wide distance between the blades caused a somewhat inhomogeneous refining result, as part of the straw remained unrefined.

### *Analysis*

Before preparing the handsheets according to the ISO 5269-1 test method, the refined pulp was wet-disintegrated according to the method ISO 5263 and screened on a Mänttä flat screen using a screen plate with a slot of 0.25 mm. Laboratory hand sheets were prepared, and paper technical properties were measured according to following test methods: bulk ISO 534:2005, tensile and strech ISO 1924-2, and Scott Bond TAPPI UM-403. The pulp was fractionated with a Bauer McNett apparatus according to SCAN-CM 6:05. The plates used were 16, 30, 100, and 200 mesh.

## Assessment of Process Concept

### *Production*

The production level was estimated for a mill utilising 100,000 tonnes of dry wheat straw. The yield of soda pulping in the calculation was 40% (Savcor Indufor 2007), the yield of ethanol production 19% (von Weymarn 2007) and the yield of chemical approach by a hot water treatment and the following alkaline peroxide bleaching 55% (Leponiemi et al. 2010; Mustajoki et al. 2010). The ethanol amount was converted to liters using a density value of 0.79 g/cm$^3$.

The yield of biogas production from dissolved solids and fines from the high temperature mechanical pulping process was derived from the experiments of Kaparaju et al. (2009). They performed a hydrothermal pretreatment at 180 to 190°C temperature for about 20 min. The biogas yield was 384 m$^3$/tonne hydrolysate or 386 m$^3$/tonne remaining solids fraction (Kaparaju et al. 2009). These pretreatment conditions resulted in a 25% dissolution of straw during this stage. Thus, the biogas yield results were assumed to be relevant for our study, and the biogas yield in it was assumed to be 385 m$^3$/tonne of dissolved solids or fines. The energy content of biogas is 6 kWh/m$^3$ (Härkönen 2008). In the “chemical” approach, only the dissolved solids from hot water treatment and the first alkaline peroxide bleaching stage are assumed to be exploitable for biogas production.

### *Pulp, ethanol, and biogas prices*

Straw pulp is not sold in the region’s commercial markets. Thus straw pulp prices were estimated based on hardwood kraft pulp prices. Savcor Indufor (2006) used an estimate of 20% lower market price for straw pulp than for corresponding hardwood market pulp in China. According to FOEX indexes Ltd., the price of hardwood kraft pulp in October 2010 was 617.5 EUR/ADt and the price of recycled fibres (OCC) was 120.2 EUR/ADt (FOEX 2010). Therefore, a reasonable estimate for the price of bleached straw soda pulp could be approximately 400 Eur/ADt and the price of the pulp produced by the "chemical" approach could be 350 Eur/ADt since the lower brightness may decrease the pulp price slightly. The price of unbleached mechanical straw pulp is estimated to vary between 150 and 250 Eur/ADt. The price spread was estimated from the fluctuation of recycled fibres price and the possible price increase of recycled fibres in the future.

Biogas prices were estimated according to current prices of natural gas and the current premium prices in some European countries where the green certificate or feed-in tariff is promoting the market introduction of green bioenergy. The biogas price is estimated to vary in the range 30 to 60 Eur/MWh.

The ethanol price was determined according to the price of Brazilian sugarcane ethanol imported to Europe and the prices of ethanol produced from renewable sources. Due to the directive on the promotion of energy from renewable sources in Europe, additional benefit is obtained when producing ethanol from wastes and residues. This next generation ethanol can be double-counted in the national quota to transportation fuels. Hence the ethanol price is estimated to vary from 0.65 to 0.98 Eur/L.

### *Investment costs*

The soda mill investment costs were assumed to be approximately the same as the kraft mill investment costs. In this study, the investment costs of the soda pulp mill were estimated to be 1700 Eur/ADt. The investment costs of the "chemical" approach were estimated to be 60% of those in the soda pulping due to the lack of chemical recovery.

The investment costs of the "mechanical" approach (unbleached pulp and energy) were estimated to be clearly lower than those of soda or "chemical" approach. The costs for the "mechanical" option were estimated from the prices of a saw dust digester, a TMP reject grinder, two-phase pressurised screens, and a biogas plant. In addition, the costs of building, engineering, and contingencies were added to the expenses.

The investment costs of a bioethanol plant using 100 000 tonnes straw were estimated based on the costs of a bioethanol plant using 160 000 tonnes straw (von Weymarn 2007) as follows,

$$I = I_{(\text{von Weymarn})} * (P / P_{(\text{von Weymarn})})^{0.7} \qquad (1)$$

where I represents the investment costs, $I_{(\text{von Weymarn})}$ is the investment cost for a 160,000 tonnes plant (110 MEur), P is the production rate for 100,000 tonnes dry straw/a, and $P_{(\text{von Weymarn})}$ is the production rate, for 160,000 tonnes dry straw/a. The annual instalment of investment costs were calculated for 10 year period and the interest rate was 5%. The repayments were assumed to be equal for each year.

### *Production costs*

The variable production costs were estimated according to West European cost level. The price of wheat straw in this calculation was 52.3 Eur/t (von Weymarn 2007). The soda mill production costs were assumed to be approximately the same as the kraft mill production costs. Staff costs were assumed to be 40 Eur/ADt for every pulping process. Maintenance costs of a biogas plant were estimated to be 15 Eur/MWh.

The chemical costs in the "chemical" process option were estimated based on the chemical consumptions from earlier research: 9% NaOH, 5% $H_2O_2$, 1% peracetic acid on dry straw (Leponiemi et al. 2010) and the following chemical prices/tonne of 100% chemical (Pirneskoski 2010): sodium hydroxide 250 €, hydrogen peroxide 475 € and peracetic acid 1850 €.

In the "mechanical" and "chemical" approach the required heating energy (kWh/ADt) of hot water treatment was calculated as follows,

$$Q = (1-\varepsilon) * \dot{m}_w * C_p * \Delta T / 3600 \qquad (2)$$

where $\varepsilon$ is the heat recovery factor, $\dot{m}_w$ is the water amount (kg), cP is the specific heat (4.19 kJ/kg°C), and $\Delta T$ is the temperature difference (°C).

The water amount was calculated as follows,

$$\dot{m}_w = \dot{m}_s * (W:S) \qquad (3)$$

where $\dot{m}_s$ is the straw amount (kg/ADt) and W:S is the water to straw ratio (kg/kg).

In the calculation, the initial temperature of the water was taken to be 40°C, the heat recovery factor 50%, and the water to straw ratio 5. The received value was multiplied with the energy cost of 30 Eur/MWh. The calculated heating energy for hot water treatment was then added to the soda pulping energy costs. The reason for adding the heating energy costs to the soda pulping energy costs was the assumption that soda cooking consumes no energy, since the energy is produced in chemical recovery and therefore the energy consumption of a soda process comes from other sub processes. It was further assumed that the energy consumption of other sub-processes in both "mechanical" and "chemical" approach is approximately at the same level as in the soda process.

## RESULTS AND DISCUSSION

### A Novel Combined Mechanical Straw Pulp and Energy Process

Previous work showed that straw pulp can be produced by hot water treatment followed by mechanical refining (Leponiemi et al. 2010). The dissolved solids and fines which hamper drainability can be utilised for energy production. The strength properties of the produced pulp were low. By further increasing the hot water treatment and refining temperature, it is possible to improve the pulp properties, as Table 1 indicates. These preliminary results show the potential of this process. The process is very simple; it requires only hot water and some mechanical energy. The straw almost defibrates by itself at 170°C; hence the mechanical energy requirements are low. The properties of such pulp are quite reasonable and therefore suitable for fluting. By an alkaline peroxide treatment, the pulp properties can be improved slightly, if needed.

**Table 1.** Pulp Properties of Mechanically Refined Hot Water Treated Wheat Straw. HWT and Refining Temperature 170 °C

| HWT and refining temperature | 120 °C<br>(Leponiemi et al. 2010) | | 170 °C | | |
|---|---|---|---|---|---|
| | Mechanically refined wheat straw | Alkaline peroxide treatment after mechanical refining | Mechanically refined wheat straw* | | Alkaline peroxide treatment after mechanical refining |
| Bulk, $m^3/t$ | 4.2 | 3.1 | 2.6 | 2.6 | 2.6 |
| Tensile index, Nm/g | 4.6 | 19.2 | 24.6 | 22.0 | 30.1 |
| Stretch, % | 1.5 | 2.1 | 1.3 | 1.4 | 2.0 |
| Scott Bond, $J/m^2$ | 44 | 95 | 141 | 122 | 188 |

* Parallel testpoints

At 170°C temperature, 30% of the straw solids were dissolved by the hot water treatment (Fig. 1). According to the Bauer-McNett fractionation, the fines content of the produced pulp was 25%. Part of the straw remained without mechanical refining effect due to the wide gap between the refiner blades. Based on the earlier results (Leponiemi et al. 2010) the fines amount would probably increase 5 to 10% if the straw was totally defibrated.

The dissolved solids and the formed fines can be used for energy production. Ethanol production could be one possibility if an ethanol plant was located close to the fibre mill. The dissolved solids and fines could presumably be utilised without a steam explosion stage, which is usually required as a pretreatment for lignocellulosics prior to fermentation. If an ethanol plant was not close to the mill, a biogas production through anaerobic digestion would be another option. In such a case the hot water treatment and mechanical refining at high temperature could presumably replace the hydrothermal pretreatment stage typically required prior to the anaerobic digestion of straw.

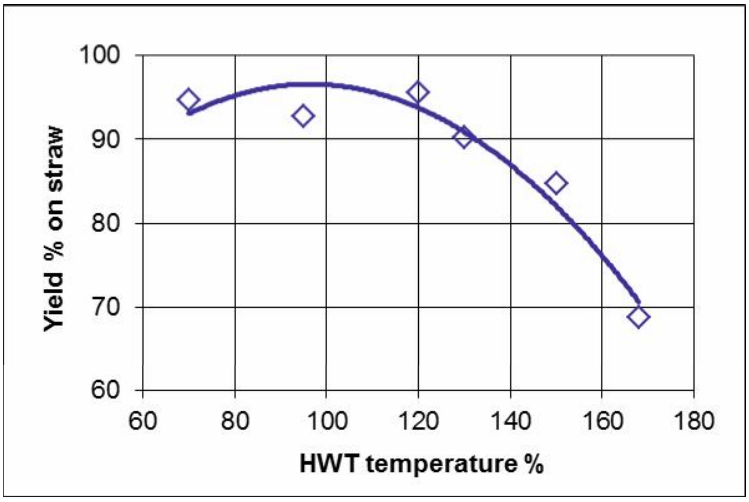

**Fig. 1.** Effect of hot water treatment temperature (HWT) on wheat straw yield

## Prefeasibility Study of Combined Pulp and Energy Production

The proposed “mechanical” process concept based on a hot water treatment and subsequent mechanical refining at high temperature could be an option for fluting production. The “chemical” approach based on a hot water treatment and subsequent alkaline peroxide bleaching (Leponiemi et al. 2010, Mustajoki et al. 2010) could be an option to replace bleached chemical pulps if very high brightness values are not required. In both approaches, the lower quality material, such as dissolved solids or fines, could be used for energy production. Soda process and ethanol production from straw were selected as reference points.

Due to the logistics involved in the use of wheat straw, the processes were restricted to approximately 50,000 ADt soda pulp/a, which means 100,000 tonnes of dry straw. The costs of the processes depend highly on the local conditions and the equipment selected. Furthermore, the prices of products depend on the market situation, and especially on the demand for the product in question. Therefore an exact evaluation is difficult to present; hence the aim of this assessment is to determine the potential of the suggested process.

Table 2 presents the pulp bioethanol and biogas production volumes from 100 000 BDt straw supply and the prices of the corresponding products. The prices are estimated according to the West European price level. The fibre losses in raw material handling and in process are assumed to be the same; thus they are not included in the assessment.

The investment costs of the “chemical” approach were estimated to be 60% lower from those of the soda pulping due to the lack of chemical recovery. The investment costs of the “mechanical” approach were estimated to be clearly lower than those of soda or “chemical” approach due to the much simpler process without chemical recovery and bleaching plant. The investment costs of a bioethanol plant were estimated to be about the same as a soda pulp mill.

**Table 2.** Pulp, Bioethanol and Biogas Production and Estimated Income. Straw Supply 100,000 BDt/a

| | **Soda** | **“Mechanical”** | **“Chemical”** | **Bioethanol** |
|---|---|---|---|---|
| **References** | (Savcor Indufor 2007) | | Leponiemi et al. 2010 | (von Weymarn 2007) |
| Pulp production ADt | **44400** | **44400** | **61100** | **0** |
| Bioethanol production, $m^3$ | | | | **24050** |
| Biogas | | | | |
| - production,million $m^3$ | | **23.1** | **9.6** | |
| - production MWh/a | | **138600** | **57800** | |
| Prices | | | | |
| - straw pulp Eur/ADt | **400** | **150-250** | **350** | |
| - ethanol, Eur/l | | | | **0.65-0.98** |
| - biogas, Eur/MWh | | **30-60** | **30-60** | |
| Income | | | | |
| - pulp, MEur/a | **17.8** | **6.7 – 11.1** | **21.4** | |
| - bioethanol, Eur/a | | | | **15.7 – 23.6** |
| - biogas, Eur/a | | **4.2 – 8.3** | **1.7 – 3.5** | |
| - Total, MEur/a | **17.8** | **10.9 – 19.4** | **23.1 – 24.9** | **15.7 – 23.6** |

The main variable production costs of pulp include raw material, chemicals, and energy. The most significant difference in production costs of a straw pulping process compared with the traditional wood based pulping processes comes from raw material costs. The soda mill production costs were assumed to be approximately the same as the kraft mill production costs. Table 3 presents the cost estimates for pulp and bioethanol production. The values are estimated according to West European cost level (Suhonen 2010).

**Table 3.** Cost Estimates for Pulp or Bioethanol Production. Straw Supply 100,000 BDt/a

| Process | **Soda** | **“Mechanical”** | **“Chemical”** | **Bioethanol** |
|---|---|---|---|---|
| Pulp production ADt/a | **44400** | **44400** | **61100** | |
| Investment costs, MEur | **75** | **23** | **45** | **79** |
| Production costs, Eur/ADt | | | | |
| - raw material | **118** | **118** | **86** | |
| - chemicals | **38** | **0** | **118** | |
| - energy | **36** | **62** | **47** | |
| - personnel | **40** | **40** | **40** | |
| - sum | **232** | **220** | **291** | |
| Production costs MEur/a | **10.3** | **9.8** | **17.8** | |
| Biogas maintenance costs, MEur/a | | **2.1** | **0.9** | |
| Bioethanol production costs | | | | |
| - Eur/l | | | | **0.55** |
| - MEur/a | | | | **13.2** |
| Total production costs, MEur/a | **10.3** | **11.9** | **18.7** | **13.2** |

## Comparison of Processes

Table 4 presents the economical comparison of the selected processes. The bioethanol production from straw is not profitable due to the high investment and production costs (von Weymarn 2007), unless the price of the produced bioethanol is significantly higher than the price of the Brazilian sugarcane ethanol. The combined production of fibres and energy by the suggested “mechanical” approach is projected to have notably lower investment costs than the soda process or a bioethanol plant. However, the value of produced unbleached pulp is lower.

**Table 4.** Profitability Calculation of Processes

| Process | **Soda** | **“Mechanical”** | **“Chemical”** | **Bioethanol** |
|---|---|---|---|---|
| Income, MEur/a | | | | |
| - pulp | **17.8** | **6.7 – 11.1** | **21.4** | |
| - biogas | | **4.2 – 8.3** | **1.7 – 3.5** | |
| - ethanol | | | | **15.7 – 23.6** |
| - sum | **17.8** | **10.9 – 19.4** | **23.1 – 24.9** | **15.7 – 23.6** |
| Costs, MEur/a | | | | |
| - interest (5%) | **3.8** | **1.2** | **2.3** | **4.0** |
| - instalment (10 years) | **7.5** | **2.3** | **4.5** | **7.9** |
| - production costs | **10.3** | **11.9** | **18.7** | **13.2** |
| - sum | **21.6** | **15.4** | **25.5** | **25.1** |
| Total | ***-3.8*** | ***-4.5 – 4.0*** | ***-2.4 – -0.6*** | ***-9.4 – -1.5*** |

The biogas production compensates for the lower pulp price; hence the process seems to have potential for further investigation. The advantage of the "chemical" approach is the clearly higher pulp yield, which increases the income from the pulp. However, at the current stage, the process consumes high amounts of chemicals, which significantly increases the production costs and environmental impact.

## Possibilities for Combined Straw Pulp and Energy Production

In Europe, the possibilities for combined straw pulp and energy production seem to be limited, unless the price of recycled paper increases above 200 Eur/Adt or significant subsidies are made to encourage bioenergy production. Then the mills which would most benefit from the cheaper raw material are the small containerboard mills with a risk of dropping out when the demand decreases. These mills typically utilise recycled fibres.

The locations of containerboard mills based on the use of recycled fibres in Europe are presented in Fig. 2. Several small-scale containerboard mills are located in France. These mills could benefit from the straw pulp use if the price was profitable. In addition, the area of agricultural land in France is over half of the land area. Hence a potentially favorable option for a combined straw and energy production in Europe could be in France.

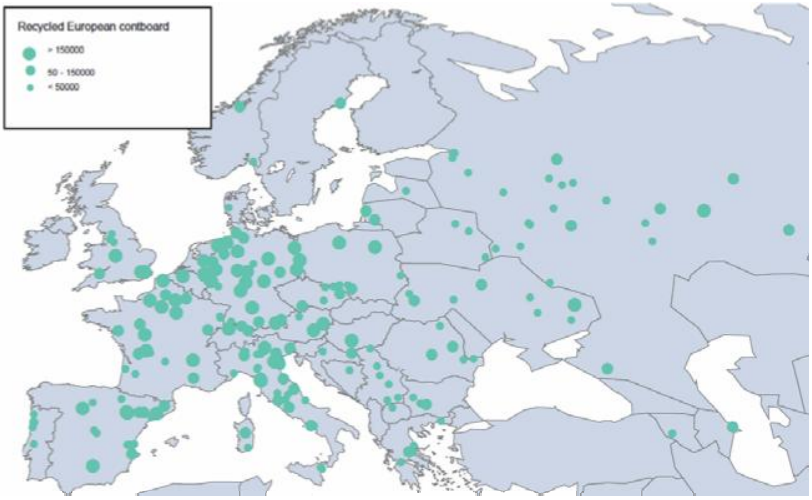

**Fig. 2.** Recycled fibre-based containerboard mills in Europe (Pöyry 2010).

In China, the chronic shortage of fibres enables the utilisation of straw as a raw material for papermaking. As the demand for fibres and renewable energy produced in an environmentally safe way is a priority in China, this fact could open possibilities to suggested combined straw pulp and energy production in a small scale if the price were acceptable.

## CONCLUSIONS

1. Adequate quality pulp for fluting production can be produced by hot water treatment and mechanical refining at a high temperature. The lower quality material, such as dissolved solids and fines, could directly be utilised for biogas or bioethanol production.
2. Due to the simple process, investment costs are moderate and chemical recovery is not needed. However, the process is economically competitive only if the price of produced pulp and biogas would be significantly higher than the current price of recycled fibres and natural gas. This indicates that subsidies may be required to promote this environmentally safe process to the markets.
3. A similar kind of hydrothermal pretreatment is needed prior to bioenergy and fibres production.
4. In Europe, suitable locations for small combined pulp and energy units are suggested to be in France. In China, they could replace environmentally acceptable smallish units without recovery or integrated with containerboard production.
5. Further research is needed to optimise the mechanical pulp production from straw by a hot water treatment and subsequent mechanical refining at a high temperature.

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Title

# Fibres and energy from wheat straw by simple practice

Abstract

The overall purpose of this work is to evaluate the possibilities of wheat straw for fibre and energy production and address the question of whether or not it is possible to develop a cost-effective process for producing good quality pulp from wheat straw for current paper or paperboard products. In addition, in light of the green energy boom, the question of whether fibre production could give added value to energy production using wheat straw is addressed.

Due to the logistics of the bulky raw material, the process should be applied on a small scale that determines the requirements for the process. The process should be simple, have low chemical consumption and be environmentally safe. The processes selected for the study were based on an initial hot water treatment. Actual defibration in the “chemical” approach was then performed using a subsequent alkaline peroxide bleaching process or in the “mechanical” approach through mechanical refining. In both approaches, energy can be produced from lower quality material such as dissolved solids or fines.

In this work, one of the primary aims besides the development of the abovementioned process is to investigate the chemical storage of wheat straw which decays easily between harvesting periods and examine its effects on pulping and pulp properties. In addition, the aim of this work is to determine the market potential for non-wood pulp and evaluate non-wood pulp production.

The results showed that the “chemical” approach produced fibres for printing and writing. The quality of the pulp was relatively good, but the chemical consumption at the target brightness of 75% was high, indicating that a chemical recovery would be needed unless the brightness target could be significantly reduced. The “mechanical” approach produced unbleached fibres for fluting and the energy production from fines and dissolved solids generated additional income. The results also showed that it is possible to store wheat straw chemically with formic acid-based chemicals over a year without significant changes in the chemical composition. The chemical storage can be integrated with the suggested chemical or mechanical defibration process, soda pulping process or any other process utilising non-wood fibres. In China, a clear demand for non-wood-based fibres exists due to a shortage of fibre and also because of the increasing demand for bioenergy. In Europe, the competitiveness of non-wood fibre utilisation will only be established if combined with energy production.

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Tekijä(t)
Anja Leponiemi

Nimeke

# Kuituja ja energiaa vehnän oljesta yksinkertaisella menetelmällä

Tiivistelmä

Tämän työn tavoitteena oli arvioida vehnän oljen käyttömahdollisuuksia kuidun ja energiantuotannon raaka-aineena sekä selvittää, onko mahdollista kehittää kustannustehokas prosessi, joka tuottaisi hyvälaatuista massaa nykyisiin paperi- tai kartonkituotteisiin ja voiko kuiduntuotanto antaa lisäarvoa vehnän oljesta valmistetun vihreän energian tuotantoon.

Vehnän oljen logistiikan vuoksi prosessin tulisi soveltua pieneen mittakaavaan, mikä aiheuttaa vaatimuksia prosessille. Prosessin tulisi olla yksinkertainen ja ympäristöystävällinen ja kemikaalikulutuksen matala. Tutkimukseen valittiin kuumavesikäsittelyyn perustuvat prosessivaihtoehdot, joissa varsinainen kuidutus tapahtuu tämän vaiheen jälkeen joko ”kemiallisesti” alkalisella peroksidivalkaisulla tai ”mekaanisesti” mekaanisella kuidutuksella. Molemmissa prosessivaihtoehdoissa energiaa voidaan tuottaa kuiduksi kelpaamattomasta materiaalista, kuten liuenneesta kuiva-aineesta tai hienoaineksesta.

Tämän työn tavoitteena oli prosessikehityksen lisäksi tutkia korjuukausien välillä helposti pilaantuvan vehnän oljen kemiallisen varastoinnin vaikutuksia massan valmistukseen ja ominaisuuksiin. Lisäksi tavoitteena oli selvittää non-wood-massan markkinapotentiaalia ja arvioida valmistetun massan tuotantoa.

Tulokset osoittivat että ”kemiallisella” prosessivaihtoehdolla voidaan tuottaa kuituja kirjoitus- ja painopapereihin. Valmistetun massan laatu oli suhteellisen hyvä mutta kemikaalikulutus 75 % tavoitevaaleuteen nähden korkea, mikä tarkoittaa, että kemikaalien talteenottoprosessi tarvitaan, ellei kemikaalikulutusta voida alentaa merkittävästi. ”Mekaanisella” prosessivaihtoehdolla voidaan valmistaa valkaisemattomia kuituja flutingin valmistukseen ja samalla saada energian valmistuksella hienoaineesta ja liuenneesta kuiva-aineesta lisätuloa.

Tulokset osoittivat myös, että vehnän olkea voidaan säilöä kemiallisesti muurahaishappopohjaisilla kemikaaleilla yli vuoden ilman merkittäviä muutoksia kemiallisessa koostumuksessa. Kemiallinen varastointi voidaan integroida esitettyyn kemialliseen tai mekaaniseen kuidutusprosessiin, soodakeittoprosessiin tai mihin tahansa prosessiin, joka hyödyntää yksivuotisia kasveja. Kroonisen kuitupulan ja lisääntyvän bioenergian tarpeen vuoksi Kiinassa on selvä tarve non-wood-kuiduille. Euroopassa non-wood-kuitujen hyödyntäminen on mahdollista vain, jos se voidaan yhdistää energian tuotantoon.

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