



Anja Leponiemi

# Fibres and energy from wheat straw by simple practice



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# **Fibres and energy from wheat straw by simple practice**

Anja Leponiemi

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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 kuumavesikäsitteilyyn 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 korjuukausiin 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 talteenotto-prosessi tarvitaan, ellei kemikaalikulutusta voida alentaa merkittävästi. ”Mekaanisella” prosessivaihtoehdolla voidaan valmistaa valkaisuamattomia kuituja flutingin valmistukseen ja samalla saada energian valmistuksella hienoaineesta ja liuenneesta kuiva-aineesta lisätuloa.

Tulokset osoittivat myös, että vehnän olkea voidaan säilöä kemiallisesti murahaishappopohjaisilla 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

- I Leponiemi, A. (2008). Non-wood pulping possibilities – a challenge for the chemical pulping industry. *Appita J.* 61(3), pp. 234–243.
- II Leponiemi, A., Johansson, A., Edelman, K. and Sipilä, K. (2010). Producing pulp and energy from wheat straw. *Appita J.* 63(1), pp. 65–73.
- 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.

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## 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 <sub>2</sub> CO <sub>3</sub>	Sodium carbonate
NSSC	Neutral sulphite semichemical process
OCC	Old corrugated containers
P	Alkaline peroxide bleaching stage
P <sub>1</sub>	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

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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).

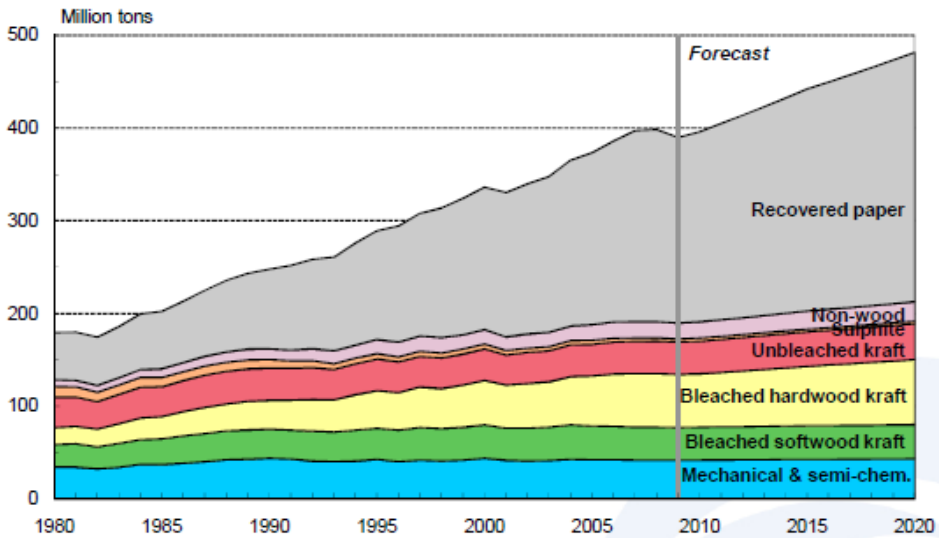


Figure 1. World consumption of papermaking fibres, 1980–2020 (Kuusisto 2010).

## 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

## 1. Introduction

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).

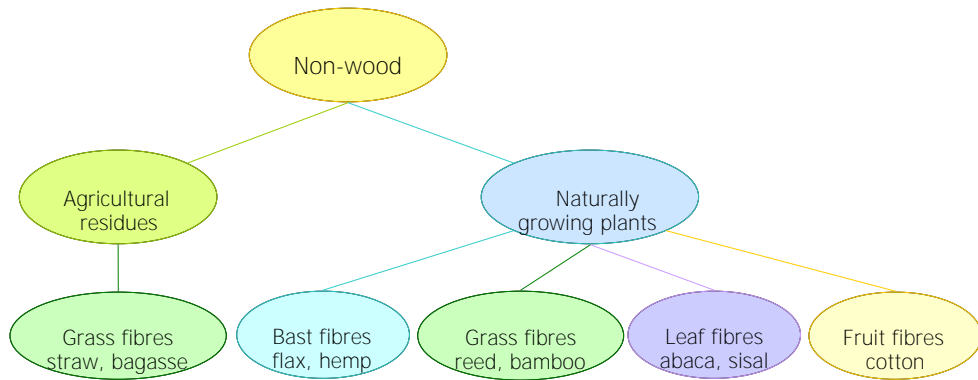


Figure 2. The classification of non-wood fibres (adapted from Ilvessalo-Pfäffli 1995).

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

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treatment is really a technical and economical challenge (Rangan & Ranganamannar 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

## 1. Introduction

(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, Edelman 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.

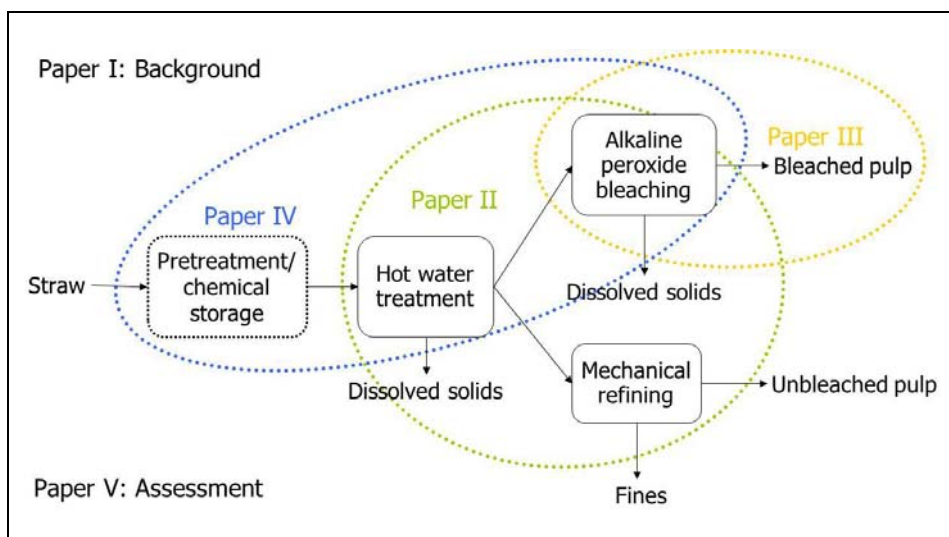


Figure 3. Overview of research plan.

#### 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.

### 3. Experimental

Table 3. Bleaching conditions of reference, pressurised P<sub>1</sub>, sugar addition and alkali pretreatment pulps. Consistency 10%, temperature in P<sub>2</sub>, Paa and P<sub>3</sub> stages 85°C, and time in P<sub>2</sub> and P<sub>3</sub> stages 180 min and in peracetic acid stage 60 min. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. PP<sub>1</sub> = pressurised P<sub>1</sub> stage, APT = NaOH pretreatment and PPT = O<sub>2</sub> pressurised NaOH pretreatment.

		Ref. bleaching	Pressurised P <sub>1</sub>	Sugar addition	Alkaline pretreatment	O <sub>2</sub> pressurised alkaline pretreatment
		Low / high chem	PP <sub>1</sub> 95°C 120 min / PP <sub>1</sub> 105°C 60 min / PP <sub>1</sub> 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 pretreatment	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 <sub>1</sub>	NaOH (%)	7.0 / 8.5	6.0 / 6.0 / 6.0	7.0 / 8.0 / 8.5	3.5 / 2.5	3.0
	H <sub>2</sub> O <sub>2</sub> (%)	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 <sub>2</sub> pressure (bar)	-	3	-	-	-
	Time (min)	60	120 / 60 / 120	60	60	60
	MgSO <sub>4</sub> (%)	-	0.3 / 0.3 / 0.3	-	-	-
	DTPA (%)	-	0.2 / 0.2 / 0.2	-	-	-
	Sugar (mg/L)	-	-	150	-	-
P <sub>2</sub>	NaOH (%)	1.0 / 1.5	1.5 / 1.0 / 1.0	1.0 / 1.0 / 1.5	0.75 / -	0.5
	H <sub>2</sub> O <sub>2</sub> (%)	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 <sub>3</sub>	NaOH (%)	1.0 / 1.5	1.0	1.0 / 1.5 / 1.5	0.75	0.75
	H <sub>2</sub> O <sub>2</sub> (%)	2.0	2.0		2.0	2.0
Acidification	SO <sub>2</sub> (%)	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<sub>2</sub>O<sub>2</sub>, 0.25% MgSO<sub>4</sub>, 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<sub>2</sub>O<sub>2</sub>.

### 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

### 3. Experimental

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 fractionated 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.

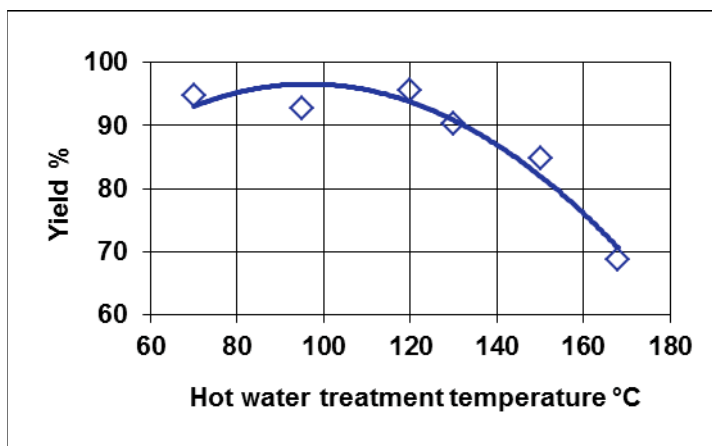


Figure 4. The effect of the hot water treatment temperature on the yield. Wheat straw 2007, time at temperature 60 min. (Paper V).

## 4. Results

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.

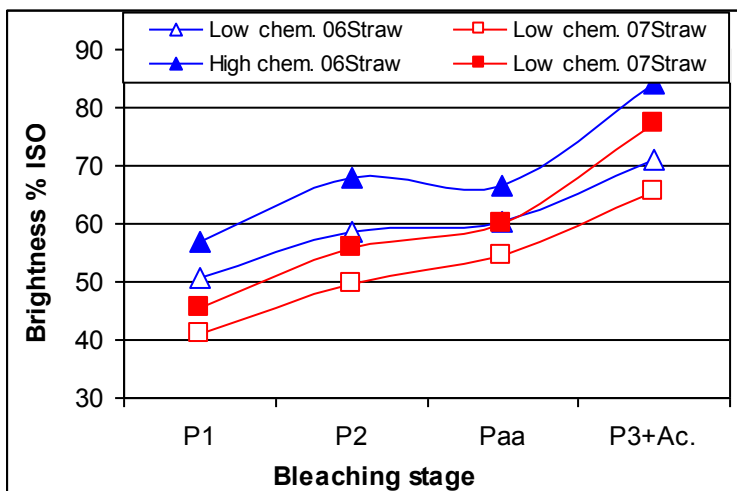


Figure 5. Brightness of reference pulps after each bleaching stage. Raw material 06Straw and 07Straw. Hot water treatment of straw at 120°C for 60 min followed by P-P-Paa-P bleaching (Paper III).

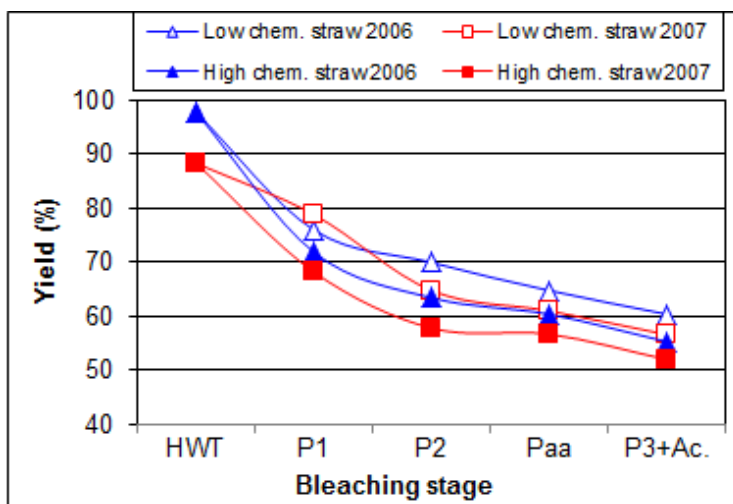


Figure 6. Yield of reference pulps after each bleaching stage; raw material 06Straw and 07Straw. Hot water treatment of straw at 120°C for 60 min followed by P-P-Paa-P bleaching (Paper III).

The process consumed high amounts of sodium hydroxide in bleaching. In practice this means that the process would need some kind of chemical recovery

#### 4. Results

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.

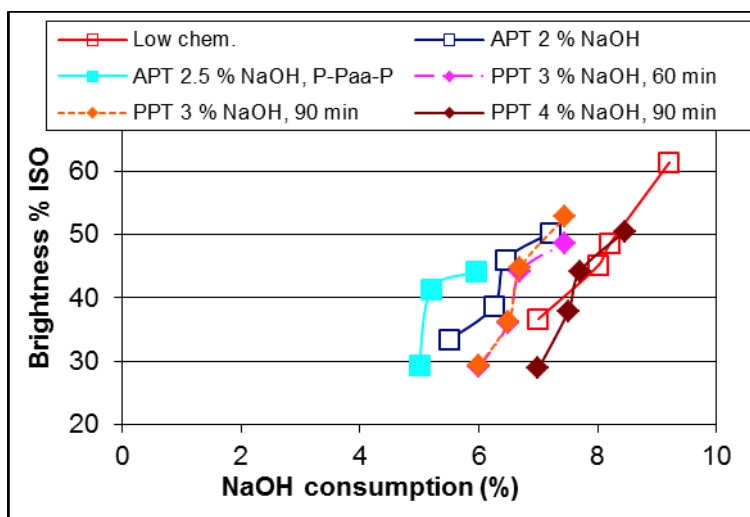


Figure 7. Brightness of alkali pre-treatment bleachings and reference pulp as a function of NaOH consumption. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by APT/PPT-P-P-Paa-P bleaching. Low chem reference pulp with 9% NaOH charge, APT alkali pre-treatment, PPT pressurised 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 <sup>2</sup> )	71.8	83.9	68.1	68.7	67.7	73.4
Thickness (µm)	112	113	109	107	107	103
Apparent density (kg/m <sup>3</sup> )	639	743	627	644	684	657
Bulk (m <sup>3</sup> /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 <sup>2</sup> /kg)	19.7	18.8	19.4	18.6	18.3	20.1
Light absorption (m <sup>2</sup> /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 <sup>2</sup> /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<sub>2</sub>CO<sub>3</sub> and the corresponding reference. The highest brightness was achieved with the 25% Na<sub>2</sub>CO<sub>3</sub> 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).

#### 4. Results

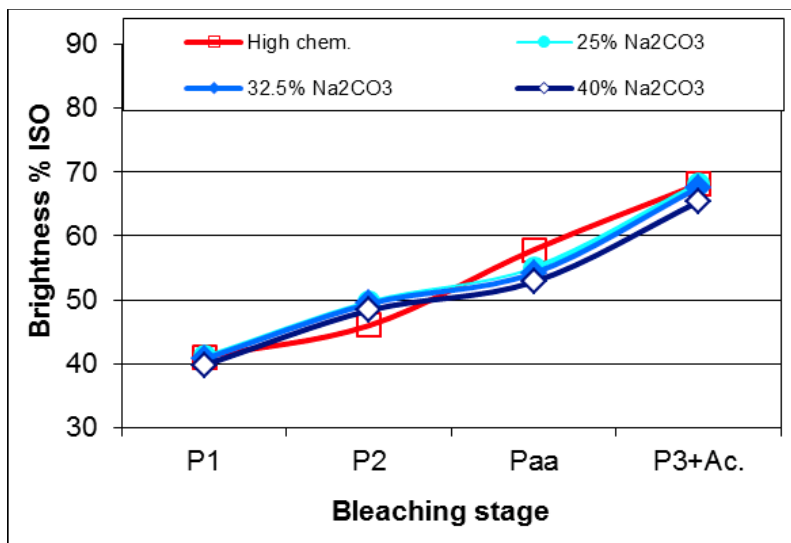


Figure 8. Brightness of sodium carbonate substitution bleaching and reference pulp after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching (Paper III).

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<sub>1</sub>) stage (Paper III). The purpose of this was to test the hypothesis about their negative effect on bleachability. However, glucose addition in the P<sub>1</sub> 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).

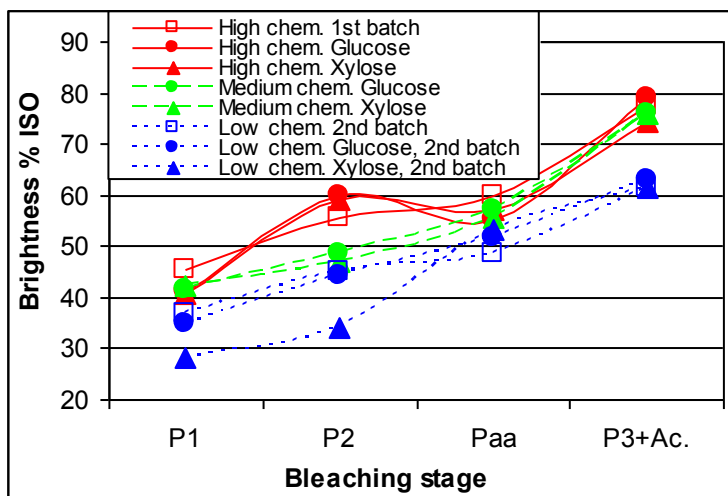


Figure 9. Brightness of sugar addition bleachings and reference pulp after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching. 1<sup>st</sup> batch = 07Straw air dried and stored in room temperature, 2<sup>nd</sup> batch = 07Straw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

#### 4. Results

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).

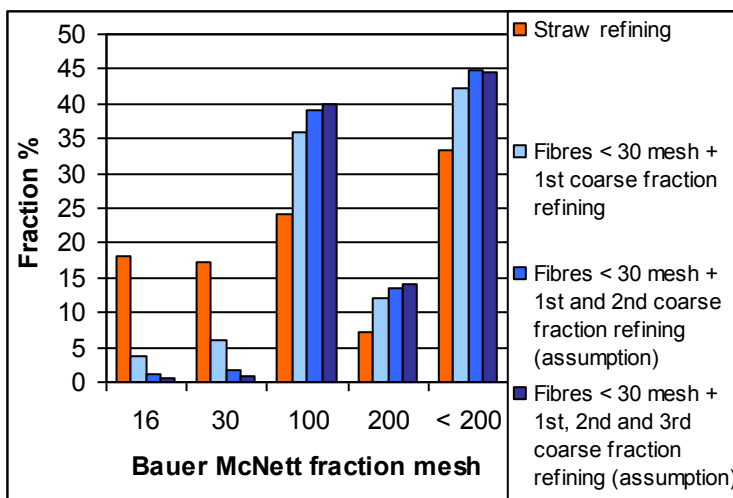


Figure 10. Mass balance of mechanically refined fibres. Estimation of coarse fibre fraction return to refining. Straw refining = fibre fractions, from refining of hot water treated straw, Fibres < 30 mesh = fibre fractions (< 30 mesh) including the sum fractions from previous refining(s) (Paper II).

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<sup>2</sup>). 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<sup>2</sup>. 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<sup>2</sup> 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<sup>2</sup>. 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

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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).

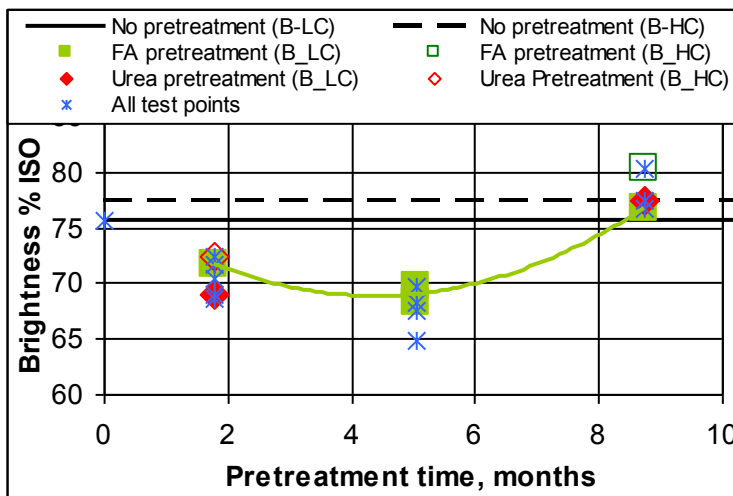


Figure 11. Final brightness as a function of straw pre-treatment time. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. P = alkaline peroxide stage, Paa = peracetic acid stage. Pre-treatment in Plexiglas acrylic silos. FA = Formic acid. B-LC = lower bleaching consistency (< 10%), B-HC =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

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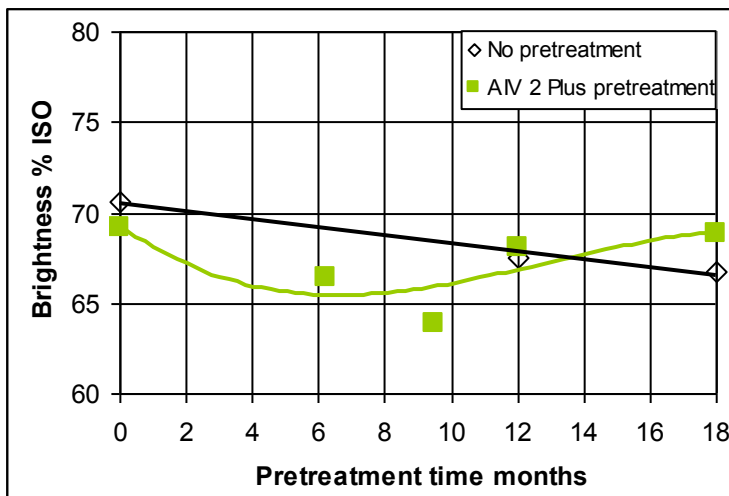


Figure 12. Final brightness as a function of straw pre-treatment time. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. Pre-treatment in round bales. Reference bales (no pre-treatment) stored in an unheated barn.

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).

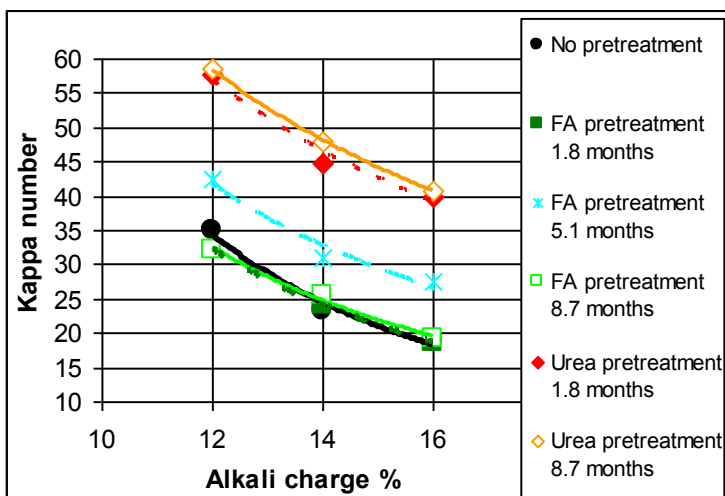


Figure 13. Kappa number as a function of straw pre-treatment time. Soda cooking at 160°C for 60 min. Pre-treatment in Plexiglas® acrylic silos (Paper IV).

## 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.

## 4. Results

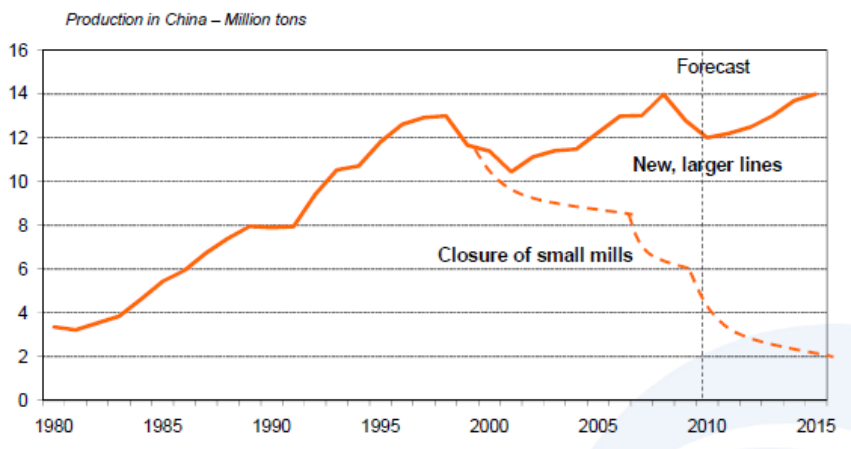


Figure 14. Future of non-wood pulp in China (Kuusisto 2010).

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.

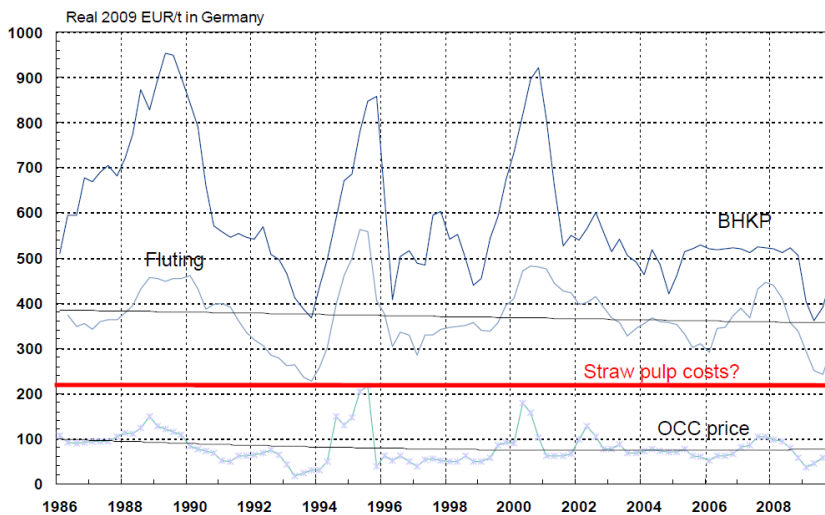


Figure 15. Real Price Development of old corrugated container (OCC) and bleached hardwood kraft pulp (BHKP) 1986–2009 (Pöry 2010).

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,

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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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VTT Publications 767  
VTT-PUBS-767

Author(s) Anja Leponiemi		
Title <b>Fibres and energy from wheat straw by simple practice</b>		
Abstract <p>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.</p> <p>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.</p> <p>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.</p> <p>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.</p>		
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VTT-PUBS-767

Tekijä(t) Anja Leponiemi		
Nimeke <b>Kuituja ja energiaa vehnän oljesta yksinkertaisella menetelmällä</b>		
Tiivistelmä <p>Tämän työn tavoitteena oli arvioida vehnän oljen käyttömahdollisuuksia kuidun ja energiantuotannon raaka-aineena sekä selvittää, onko mahdollista kehittää kustannustehokas prosessi, joka tuottaisi hyvälaatuisia massaa nykyisiin paperi- tai kartonkituotteisiin ja voiko kuiduntuotanto antaa lisäarvoa vehnän oljesta valmistetun vihreän energian tuotantoon.</p> <p>Vehnän oljen logistiikan vuoksi prosessin tulisi soveltua pieneen mittakaavaan, mikä aiheuttaa vaatimuksia prosessille. Prosessin tulisi olla yksinkertainen ja ympäristöystävällinen ja kemikaalikulutuksen matala. Tutkimukseen valittiin kuumavesikäsitteilyyn perustuvat prosessivaihtoehdot, joissa varsinainen kuidutus tapahtuu tämän vaiheen jälkeen joko "kemiallisesti" alkalisella peroksidivalkaisulla tai "mekaanisesti" mekaanisella kuidutuksella. Molemmista prosessivaihtoehdoissa energiaa voidaan tuottaa kuiduksi kelpaamattomasta materiaalista, kuten liuenneesta kuiva-aineesta tai hienoaineksesta.</p> <p>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.</p> <p>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 talteenotto prosessi tarvitaan, ellei kemikaalikulutusta voida alentaa merkittävästi. "Mekaanisella" prosessivaihtoehdolla voidaan valmistaa valkaisuomattomia kuituja flutingin valmistukseen ja samalla saada energian valmistuksella hienoainesta ja liuenneesta kuiva-aineesta lisätuloa.</p> <p>Tulokset osoittivat myös, että vehnän olkea voidaan säilöä kemiallisesti muurahaispohjaisilla 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.</p>		
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