MANUFACTURE OF STRAW MDF AND FIBREBOARDS

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ABSTRACT

The purpose of this thesis was to develop an economical, sustainable, and environmentally friendly straw Medium Density Fibreboard (MDF) process, capable of full-scale manufacturing and to produce MDF of requested quality. The investigated straw was based on wheat (*Triticum aestivum* L.) and rice (*Oryza sativa* L.). In this thesis three different methods were taken for manufacture of straw MDF; (A) wheat-straw fibre was blowline blended with melamine-modified urea-formaldehyde (MUF), (B) rice-straw fibre was mixed with methylene diphenyl diisocyanate (MDI) in a resin drum-blender, and (C) wheat-straw fibre was activated in the blowline by the addition of Fenton’s reagent (H$_2$O$_2$/Fe$^{2+}$) for production of non-resin MDF panels. The MUF/wheat straw MDF panels were approved according to the requirements of the EN standard for MDF (EN 622-5, 2006). The MDI/rice-straw MDF panels were approved according to requirements of the standard for MDF of the American National Standard Institute (ANSI A208.2-2002). The non-resin wheat-straw panels showed mediocre MDF panel properties and were not approved according to the requirements in the MDF standard. The dry process for wood-based MDF was modified for production of straw MDF. The straw MDF process was divided into seven main process steps.

1. Size-reduction (hammer-milling) and screening of straw
2. Wetting and heating of straw
3. Defibration
4. Resination of straw fibre
5. Mat forming
6. Pre-pressing
7. Hot-pressing
The primary results were that the straw MDF process was capable of providing satisfactory straw MDF panels based on different types of straw species and adhesives. Moreover, the straw MDF process was performed in pilot-plant scale and demonstrated as a suitable method for producing straw MDF from straw bales to finished straw MDF panels. In the environmental perspective the agricultural straw-waste is a suitable source for producing MDF to avoid open field burning and to capture carbon dioxide (CO₂), the biological sink for extended time into MDF panels, instead of converting straw directly into bio energy or applying straw fibre a few times as recycled paper. Additionally, the straw MDF panels can be recycled or converted to energy after utilization.

A relationship between water retention value (WRV) of resinated straw fibres, the thickness swelling of corresponding straw MDF panels, and the amount of applied adhesive was determined. WRV of the straw fibre increased and the TS of straw MDF declined as a function of the resin content. The empirical models developed were of acceptable significance and the R² values were 0.69 (WRV) and 0.75 (TS), respectively. Reduced thickness swelling of MDF as the resin content is increased is well-known. The increase of WRV as a function of added polymers is not completely established within the science of fibre swelling. Fortunately, more fundamental research can be initiated and likely a simple method for prediction of thickness swelling of MDF by analysis of the dried and resinated MDF fibres is possible.

Keywords: Rice, Wheat, Straw, MDF, HDF, UF, MUF, MDI, Non-resin, binderless MDF, Ash, Silicon, SEM, Hot-pressing, MOR, MOE, IB, Thickness swelling, MDF properties; fibre swelling, WRV, Refining, Defibration.
SAMMANDRAG

Syftet med denna avhandling var att lägga grunden för en ekonomisk, hållbar och miljövänlig MDF process för halmrävara, kapabel för fullskalig produktion av MDF och goda skivegenskaper. Framställningen av MDF skivor utgick från halm av vete (*Triticum aestivum* L.) och ris (*Oryzae sativa* L.). Tre olika metoder användes för att producera MDF av halm; (A) fibrer av vetehalm belimmades i blåsledning med ett melaminmodifierat urea-formaldehydlim (MUF), (B) fibrer av rishalm belimmades i en limblandare med metylen difenyl diisocyanate (MDI), (C) Limfria MDF skivor av vetehalm framställdes med aktivering av fibrer genom tillsats av Fenton’s reagens (H₂O₂/Fe²⁺) i blåsledning utan någon tillsats av syntetiskt lim. Sammanfattningsvis kan det understrykas att framställda MDF-skivor av MUF/vetehalm var godkända enligt standard för MDF (EN 622-5, 2006). Dessutom var framställda MDF skivor av MDI/rishalm också godkända enligt krav i standard för MDF ”American National Standard Institute” (ANSI A2008.2-2002). Limfria vete halmskivor visade på måttliga skivegenskaper och klarade inte kraven i MDF standard.

Fiberframställningsprocessen för MDF modifierades till en produktion utgående från halm. MDF processen för halm delades upp i sju primära processoperationer.

1. Storleksreducering och sällning av halm
2. Vätning och uppvärmning av halm
3. Defibrering
4. Belimmning av halmfiber
5. Mattformning
6. Förpressning
7. Fressning

Ett förhållande mellan “water retention value” (WRV), av belimmade halmfiber, tjocklekssvällning för motsvarande MDF av halmskivor och mängden av tillsatt lim vid olika nivåer har undersöks. Med ökande limhalt tilltog WRV fibersvällning, vidare minskade tjocklekssvällning för motsvarande MDF skivor. De framtagna empiriska modellerna var godtagbara och beräknade $R^2$ värden var 0.69 (WRV) och 0.75 (TS). Minskad tjocklekssvällning med ökad limhalt är dokumenterad sen tidigare. Ökad fibersvällning WRV vid tillsats av polymerer (limmer) är inte fullständigt etablerad inom vetenskapen för fibersvällning. Lyckligtvis kan grundläggande forskning initieras och sannolikt föreligger en enkel metod för att prediktera tjocklekssvällning av MDF genom analyser av torkade och belimmad MDF fiber.
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LIST OF PAPERS

This thesis is mainly based on the following four papers, herein referred to by their Roman numerals:

Paper I Properties of medium-density fibreboards based on wheat straw and melamine-modified urea-formaldehyde (UMF) resin
Halvarsson, S., Edlund, H., Norgren, M.

Paper II Manufacture of non-resin wheat-straw fibreboards
Halvarsson, S., Edlund, H., Norgren, M.

Paper III Manufacture of High-Performance Rice-Straw Fibreboards
Halvarsson, S., Edlund, H., Norgren, M.

Paper IV Wheat-straw as a raw material for manufacture of straw MDF
Halvarsson, S., Edlund, H., Norgren, M.
BioResources 2010, 5(2), 1215-1231.
RELATED PAPERS

The related papers are the author’s contribution to conferences and symposia.

Manufacturing of fiber composite medium density fiberboards (MDF) based on annual plant fiber and urea formaldehyde resin
Halvarsson, S., Norgren, M., Edlund, H.

Processing of wheat-straw materials for production of medium density fibreboard (MDF)
Halvarsson, S., Edlund, H., Norgren, M.

How to produce high performance straw MDF
Halvarsson, S., Edlund, H., Norgren, M.
1. INTRODUCTION

The global occurrence of wood-based lignocellulosic fibre is still adequate and there is today no general fibre shortage or crises. Yet at the same time, we have some regional deficiency of wood-based fibres. Industrial demand of proper wood-based raw materials is critical in several Asian countries. The strong economic growth in Asia has contributed to increased demand of wood-based raw materials. Wood-based biomass is becoming more restricted and expensive for producers of pulp & paper, bio-energy, lumber, and wood-based composite fibreboards. Moreover, the increasing environmental awareness and concerns of the health of forests, wildlife diversity, biomass productivity, climate, and the biological sink directs research to alternative fibre recourses. Annual plant materials are promising candidates for alternative lignocellulosic fibre composites. Several annual plant fibres such as flax, hemp, jute, kenaf, bagasse, corn, and bamboo have been the subject of extensive research for the manufacture of non-wood particle and fibreboards (Rowell, 1996; Youngqvist et al., 1996; Rowell and Rowell, 1997; Hague et al., 1998; Rowell, 2001). Agricultural crop residues such as cereal straws, i.e. wheat, barely, oats, rye, and rice are essential for the growth of grains and produced in billions of tonnes around the world. The agro-straw materials are abundant, inexpensive, and readily available sources of lignocellulosic fibres. The basic challenge for board producers is to convert the agricultural straw materials into particle boards (PB), medium density fibreboards (MDF), or high density fibreboards (HDF) in a sound technical and economical process (Sauter, 1996; Eroglu and Istek, 2000; Han et al., 2001b; Xing et al., 2006; Halvarsson et al., 2008, 2009, 2010a, b).

In this thesis the manufacture of non-wood high-performance (MDF/HDF) is investigated on wheat and rice-straw. Different types of adhesives, urea-formaldehyde (UF), melamine-modified urea-formaldehyde resins (MUF), and methylene diisocyanate (MDI) were evaluated in pilot-scale. Moreover, binderless (non-resin) wheat-straw fibreboards have been produced by activation of straw fibres by addition of hydrogen peroxide (Fenton’s reagent).

The conventional type of composite fibreboards consists of refined (defibrated) wood fibres glued together by a thermosetting adhesive (Rhodes and Gehrts, 1995). The most common adhesives in the wood-based fibreboard industry are based on formaldehyde, urea-formaldehyde (UF), melamine-modified urea-formaldehyde (MUF) and phenol-formaldehyde (PF) resins (Pizzi, 1983; Ernst, 1997; Xing et al., 2006). The fibreboards are generally recognized as MDF or HDF. However, other types of fibreboards known as Hard Board (HB) or Masonite
boards are also manufactured. Masonite boards were one of the first commercial fibreboards (Mason, 1927). In this early wet-process, wood fibres were generated by steam explosion of wood chips and pressed to fibreboards without addition of adhesive. During hot pressing softening of the lignin and self-bonding between fibres contribute to the final formation of the fibreboards. The drawbacks of this type of fibreboard (hardboard) processing include high water consumption, dark colour of the boards and long pressing times. The development of the hardboard process has been directed into the more modern dry process method and synthetic adhesive is normally added.

1.1. Definition of fibreboard

The methods of manufacture of wood-based fibreboard are generally divided into the wet and dry methods. The definitions of fibreboards are formulated in the European standard (EN 622-5, 2006). Originally, fibreboards are classified by their production process as follows:

- Wet process fibreboards (fibre distribution in water)
- Dry process fibreboards (fibre distribution in air)

Wet process boards are fibreboards having fibre moisture content (MC) of more than 20% at the stage of forming. Additionally, wet process boards are classified according to density, as follows:

- Hardboards (HB): Boards with a density ≥ 900 kg/m³
- Medium boards (MD): Boards with a density ≥ 400 kg/m³ to < 900 kg/m³

Wet process hardboards use water as the distribution medium for the fibres to be formed into a mat. This method is an extension of paper manufacturing. Dry process fibreboards (MDF) having a fibre moisture content of less than 20% at the stage of forming, and having a density ≥ 450 kg/m³. These boards are essentially produced under heat and pressure with the addition of a synthetic adhesive. For marketing purposes, MDF of specific density range can be given different denominations. For example, the following density-related marketing terms for MDF have become established:

- HDF: MDF with a density ≥ 800 kg/m³
- Light MDF: MDF with a density ≤ 650 kg/m³
- Ultra-light MDF: MDF with a density ≤ 550 kg/m³
In this work the more modern dry fibreboard method is applied and described for wood- and straw-based fibreboards. The density range of produced straw fibreboards is in the range of 650–1100 kg/m$^3$ and according to the above definitions of MDF and HDF types.

1.2. Manufacture of MDF/HDF

The manufacture of composite fibreboard or MDF is based on several different and complex processing steps. The raw material is size-reduced, screened, washed (cleaned), heated, refined to fibres of sufficient quality and capacity to fulfil the physical, chemical, and economical requirements of the finished fibreboard composite product (Ernst, 1997). Thermo-setting adhesive (resin) is added in a tube (blowline) after defibration or sprayed after fibre drying in a resin drum-blender to glue the fibres together in subsequent hot-pressing (Gran, 1982). The range of UF-adhesive is 3–18% depending on type of selected resin and desired MDF-properties. MDI resin is added in much lower amounts and in the range of 3–6%. Two principles of resination can be observed in the MDF process. The most common method is the blowline blending method; resin is added into the blowline before drying. The second method of applying resin is performed after the fibre drying process and resin is sprayed on the fibre in a special blending unit. The blowline blending method provides a better resin distribution on the fibre and the separate resin blending method (after the drying) shows in general lower resin consumption but at a higher risk of resin spots on the finished MDF panels.

The resinated fibres are dried to MC in the range of 8–12%. The dry and resinated fibre is then followed by sifting, mat forming and pre-pressing operations. Hot-pressing of the fibre mat involve curing of the added adhesive and compression/consolidation of the fibre mat to defined thickness and density of the wood fibre composite. After cooling the fibreboards are cut, sized, and sanded.

The processing of straw differs from that of wood in the first part of the MDF production. The starting raw materials for wood-based MDF are lumber or timber logs that are debarked, chipped, screened, and washed before the introduction into the defibration process. The preparation of waste straw materials starts directly after harvesting. Straw must be dried to MC levels below 18% to reduce the risk of microbiological degradation. The waste straw is either stored in bales or can be handled as loose straw. One unique challenge of handling straw in large-scale production is the logistic and storing in dry conditions for long time-periods. Straw is an annual plant and is only harvested once or perhaps two times a year. The storage at comparative larger areas and longer time periods than wood-based materials is necessary. In wet conditions special attention must be paid since the
straw will deteriorate by microbiological attack, fungus, and exposure to day-light. Fortunately, the straw-based raw materials can be stored for several years at dark, cool, and dry-conditions without any major deterioration.

The dried straw consists of leaves, neds, internodes, and a high amount of non-fibrous components that degrade in the milling process. The straw material is sized-reduced by chopping and/or hammer-milling. The size-reduction processes involve fabrication of shorter straw components 10 – 50 mm in length, dust and small-particles. The most valuable fibre components are found in the tube like straw component (internode). The internodes have an useless outer layer (epidermis) consisting of high amounts of silicon in the form of micro-sized particles or microfossils (phytoliths) (Milowych et al., 1996; Ball et al., 1999). It is of importance to remove dust and straw fragments for reduction of the amount of silicon and other inorganic components which have negative effects on the straw MDF process. Moreover, lower resin consumption or fibre quality is beneficial for the removal of small particles and dust.

2. LIGNOCELLULOSIC MATERIAL AND STRAW STRUCTURE

Lignocellulosic materials are non-expensive, accessible, renewable, and fundamental resources of great human importance. Typical examples are lumber, boards, paper, and fibreboards. Three main chemical components of the fibre plant cell wall are essential for the physical strength and chemical structure; cellulose, hemicellulose, and lignin. Moreover, pectins and extractives are also present in plants but at lower levels. The three basic chemical components are synthesised in the nature from water, carbon dioxide, and sunlight as the required energy source.

2.1. Cellulose

Cellulose is a linear homo-polysaccharide that consists of β-D-glucopyranose (glucose) units linked together by β-D-(1-4) links. This polysaccharide is widespread in nature, occurring in both primitive and highly complex plants. The size of a polymer or a macromolecule is defined as the degree of polymerisation (DP) in a single chain. The DP of cellulose is of 10 000 size and above. However, conformational analysis of cellulose indicated that cellubiose (4-O-β-D-glucopyranosyl-β-D-glucopyranose) rather than glucose is its basic repeating unit of the polysaccharide, see Figure 2.1-1. Due to the linearity of the cellulose backbone, adjacent polymer chains forms a framework of water insoluble aggregates of varying length and width. These elementary micro fibrils contain
both highly ordered (crystalline) and disordered (amorphous) regions (Lennholm and Henriksson, 2007).

Figure 2.1-1 Structure of cellulose. Anhydroglucose is the monomer of cellulose, cellobiose is the dimer. The repeated unit in cellulose is a cellobiose residue rather than a glucose unit (Lennholm and Henriksson, 2007).

2.2. Hemicellulose

Hemicelluloses are plant hetero-polysaccharides whose chemical nature varies from tissue and from species to species and even in different types of cells within the same plant. These polysaccharides are formed by a wide variety of building blocks including pentones, hexoses, and uronic acids. Several classes of hemicellulose can be identified; (a) unbranched polymers such as (1-4) – linked xylans or mannans, (b) helical polymers such as (1-3) – linked xylans, (c) branched polymers such as (1-4) – linked galactoglucomannans, and (d) pectic substances such as polyramnogalacturonans. Hemicelluloses are structurally more related to cellulosics than lignin and are deposited in the cell wall at an earlier stage of biosynthesis (Teleman, 2007). Despite the complexity of these polysaccharides, their structure seems to be rodlike with branches and side chains folded back to the main chain by means of hydrogen bonding. This rodlike structure contributes to an interaction with cellulose, resulting in a tight association that create a high stability to the formed aggregate, see Figure 2.2-1. Schroeder investigated the swelling and shrinking of hardwoods (HW) and softwoods (SW). HW and SW have about the same amount of cellulose, but they differ in the amount of lignin and hemicellulose. HW species average less lignin than SW species; 22 and 28%, respectively. Hemicellulose in hardwoods is in average 5% higher than softwoods. Hardwoods generally shrink and swell more than softwoods (Schroeder, 1972).
2.3. Lignin

Lignin is the natural glue between fibres in wood and annual plants. As a major cell wall component, lignin provides rigidity, internal transport of water and nutrients and protection against attack by microorganisms. Lignin is simplified as an amorphous polymer consisting of phenylpropane units, and their precursors are three aromatic alcohols (monolignols) (Figure 2.3-1) specifically, (1) p-coumaryl, (2) coniferyl, and (3) sinapyl alcohols. The respective aromatic constituents of these alcohols in the polymer are called p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) moieties (Lewis and Yamamoto, 1990). All types of plant lignins are composed of these three phenyl propane units. Lignin in softwood is mainly composed of guaiacyl. The hardwood lignin is dominated by guaiacyl and syringyl moieties. However, the lignin structure observed in annual plant materials (grass) differ and the occurrence of hydroxyphenyl in the lignin structure is notable (Buranov and Mazza, 2008). Lignin does not exist in plant tissue as an independent polymer but it is bonded with other polymers, cellulose and hemicellulose forming complexes with them. Lignin is always associated with hemicelluloses, not only as physical admixtures, but through covalent bonds (Sarkanen and Ludwig, 1971).
The link between lignin and hemicelluloses is always associated with carbohydrates via covalent bonds at two sites: α-carbon and C-4 in the benzene ring, and this association is called lignin–carbohydrate complexes (LCC). In herbaceous plants, hydroxycinnamic acids (p-coumaric and ferulic acids) are attached to lignin and hemicelluloses via ester and ether bonds as bridges between them forming lignin/phenolics–carbohydrate complexes (Baucher et al., 1998; Sun et al., 2002). Because of this chemical nature of the lignin, it is practically impossible to extract lignins in pure form.

The lignin–carbohydrate complexes from herbaceous crops are structurally different from those in woods and contain ferulic bridges between lignin and carbohydrates (arabinoxylans) via ester-linked ferulic acids (Himmelsbach et al., 1998).
Therefore, they are often referred to as “lignin/phenolics–carbohydrate” complexes (Figure 2.3-3). Ferulic acid is attached to lignin with ether bonds and to carbohydrates with ester bond. Ester linkages between p-coumaric and ferulic acids and lignin have been confirmed in milled wood lignin of grasses by analytical and spectrophotometric procedures (Higuchi et al., 1967).

2.4. Structure of straw

Annual plants as wheat and rice-straw are less homogenous than the perennial softwoods or hardwoods in the morphological structure. The straw is the structural material that makes the plant to stand up and is composed of the stem and leaves; the stem is divided into nodes and internodes, and the internodes are separated by the nodes at which the leaves are attached, see anatomy of a wheat plant in Figure 2.4-1.

![Anatomy of the wheat plant](image)

The internodes are the parts containing fibres of sufficient amount and quality that are of interest for refining and manufacture of MDF. Nodes and leaves contain less amounts of fibre cell elements and are rather useless as a fibre raw material after the thermo-mechanical defibration process. Most of those unsatisfactory plant components contain thin-walled non-fibrous cell elements and deteriorate fast in the thermo-mechanical processing. Refining of straw material will always generate cell fragments, dust, and fines. In wheat-straw the fibre part is around 67% and for rice-straw the fibrous tissue is estimated to 46% (Jin and Chen, 2007). Compared to wood the fibrous fraction is in the range of 73 – 98%. The outer part of the straw
and leaves (epidermis) is enriched by a waxy layer and contain inorganic substances, silicon (opal silica), (Jones and Milne, 1963; Jones et al., 1963; Inglesby et al., 2005). This outer layer of straw corresponds to bark (perdermis) for wood species. Wetting of untreated straw and applying water-based adhesives to chopped straw units are considered as major problems in the particleboard industry (Markessini et al., 1997; Mo et al., 2003).

The wheat-straw stem is comprised of several internodes and nodes. One example is the winter wheat, Washington State, USA, Madsen type, which contain 4 internodes and 3 nodes in the stem (McKean and Jacobs, 1997). The length of the different internodes varies along the height of the stem and the internode length increases from the ground to the top. The physical structure and chemical composition of the internodes and nodes are consequently depending on the position in the stem. The amount of the main chemical components as cellulose, hemicellulose, and lignin vary within the straw length. The cellulose content is lower and the lignin content is higher at the ground level of the wheat-straw compared with the top part. Compositions of the main chemical substances changes between and within the different parts of the wheat plant. The internodal sections contain more cellulose than the leaves. Both (Jacobs et al., 2000) and (Wisur et al., 1993) observed higher cellulose content in the internodes compared with other straw components. Chemical data varies from plant to plant, and within different parts of the same plant (Billa and Monties, 1995; Papatheofanous et al., 1998). The variations will also depend on different geographic locations, ages, climate, and soil conditions. The analysed straw species have a natural variation of the chemical composition. Moreover, it is important to know the origin of the botanical part and the procedure used in the analysis to get a correct chemical map of the raw material.

The amounts of cellulose and lignin are in general lower in straws than in wood. Consequently, the amount of hemicellulose is higher (Lawther et al., 1995; Rowell and Rowell, 1997; Schmidt et al., 2002). A more hydrophilic characteristic of the refined straw fibres is expected compared with wood-based fibres. However, the largest difference in the chemical characteristic of straw compared with wood-based material is the high amount of minerals and the ash content in straw. In rice-straw ash contents of up to 20% have been observed. Ash content of wheat-straw is in the range of 5 – 10%. The measured ash content in wood is below 0.5%.

The optimal straw material for the fibreboard and paper producing industries is obviously the straw internodes. Two straw species of industrial interest are rice and wheat-straw. Wheat-straw contains a higher content of cellulose and less
silicon substances than rice-straw and thus more favourable for the pulp and paper industry. However, for the fibreboard manufacture a mechanical strong fibre and a high fibre yield is of interest and the two different straw species are almost of the same importance in this respect.

2.4.1. The straw morphology

Investigations of rice and wheat-straw morphology have exposed a complex structure of several different cell elements, parenchyma, vascular bundles, epidermis, and the fibre cells (Figure 2.4-2). The outer part of the straw (epidermis) contain wax and inorganic substances on the surfaces, and then follows a region with fibre bundles (vascular bundles) integrated in a region of parenchyma and vessel elements. The inside of the tubular straw (lumen) is delimited by the pithy lining (White and Ansell, 1983; Yu et al., 2005; Yu et al., 2008). A cross-section of a wheat-straw internode is shown in Figure 2.4-2. The largest amount of valuable fibres and the most useful part of the straw for production of fibreboards was found in the internodes. Jacobs reported that wheat-straw displayed a variation of fibre length for different internodes (Jacobs et al., 2000). The fibre lengths were somewhat shorter in the top internode compared with the ground level of the straw. Moreover, the amount of fibres in the different straw parts; internodes, nodes; and leaves are of various levels.

Unlike wheat, the cross-section of rice-straw reveals a different type of ultrastructure, beside the tubular concentric ring structure the centre of the rice-straw internodes contains a core (Figure 2.4-3 and 2.4-4). Moreover, rice is an aquatic plant and has a different type of protecting layer, including substances composed of lignin, amorphous silica, and other inorganic substances.
Figure 2.4-3 SEM micrograph of a cross section of the wheat-straw internode, (a) epidermis, (b) parenchyma, (c) lumen, (d) vascular bundles (Yu et al., 2008).

Figure 2.4-4 SEM micrograph of a cross-section of a rice-straw internode (Reddy and Yang, 2006).
The different types of fibres, micro fibres and single cell are shown in Figure 2.4-5. These fibres and bundle of fibres will be the basic component in the produced straw MDF.

Figure 2.4-5  SEM micrograph of the (a) wheat-straw cross-section, (b) microfibers and (c) TEM images (magnification x 15,000) of the wheat-straw nanofibre adapted from (Alemdar and Sain, 2008).
The fibre type and fibre length is of great importance when processing straw fibre and other lignocellulosic fibre. The length and width of some lignocellulosic fibre is presented in *Table 2.4-1*.

*Table 2.4-1*

*Dimensions and chemical composition of lignocellulosic fibres (Rowell, 2001)*

<table>
<thead>
<tr>
<th>Type of Fibre</th>
<th>Cellulose [%]</th>
<th>Lignin [%]</th>
<th>Fibre-length Mean [mm]</th>
<th>Dimension Width Mean [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>32-37</td>
<td>18-26</td>
<td>1.7</td>
<td>0.020</td>
</tr>
<tr>
<td>Cereal-straw</td>
<td>31-45</td>
<td>16-19</td>
<td>1.5</td>
<td>0.023</td>
</tr>
<tr>
<td>Corn-straw</td>
<td>32-35</td>
<td>16-27</td>
<td>1.5</td>
<td>0.018</td>
</tr>
<tr>
<td>Wheat-straw</td>
<td>33-39</td>
<td>16-23</td>
<td>1.4</td>
<td>0.015</td>
</tr>
<tr>
<td>Rice-straw</td>
<td>28-36</td>
<td>12-16</td>
<td>1.4</td>
<td>0.008</td>
</tr>
<tr>
<td><strong>Wood-based</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Softwood</td>
<td>40-45</td>
<td>26-34</td>
<td>4.1</td>
<td>0.025</td>
</tr>
<tr>
<td>Hardwood</td>
<td>38-49</td>
<td>23-30</td>
<td>1.2</td>
<td>0.030</td>
</tr>
<tr>
<td><strong>Annual plants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cotton</td>
<td>85-90</td>
<td>0.7-1.6</td>
<td>25</td>
<td>0.020</td>
</tr>
<tr>
<td>Seed Flax</td>
<td>43-47</td>
<td>21-23</td>
<td>30</td>
<td>0.020</td>
</tr>
<tr>
<td>Hemp</td>
<td>57-77</td>
<td>9-13</td>
<td>20</td>
<td>0.022</td>
</tr>
<tr>
<td>Abaca</td>
<td>56-63</td>
<td>7-9</td>
<td>6.0</td>
<td>0.024</td>
</tr>
<tr>
<td>Bamboo</td>
<td>26-43</td>
<td>21-31</td>
<td>2.7</td>
<td>0.014</td>
</tr>
<tr>
<td>Kenaf</td>
<td>44-57</td>
<td>15-19</td>
<td>2.6</td>
<td>0.020</td>
</tr>
<tr>
<td>Jute</td>
<td>45-63</td>
<td>21-26</td>
<td>2.5</td>
<td>0.020</td>
</tr>
<tr>
<td>Papyrus</td>
<td>38-44</td>
<td>16-19</td>
<td>1.8</td>
<td>0.012</td>
</tr>
</tbody>
</table>

The length of straw fibres is shorter than softwood fibres but is in the same level as hardwood fibres. The amount of lignin and cellulose is also lower than both HW and SW according to *Table 2.4.1*. Some of the annul plants displayed very long fibre length and were above 20 mm for Cotton, Seed Flax, and Hemp.
The leaf and stem for all of the cereal straws are in principle designed in a multilayered structure as shown for barely straw in Figure 2.4-6. The top layer is a cuticle, which is defined as the continuous non-cellular membrane lying on the epidermal walls. The estimated cuticle thickness is generally 1 μm and contains a wax layer in the form of an unspecified thin film or characteristic wax crystals. The cuticular waxes are formidable barriers of the straw plants to control the exchange of water, solutes, and even gases and vapours (Wisniewska et al., 2003). Cuticular waxes are believed to cover only the outer part of a stem or leaves. Moreover, the wax crystals are represented of different shapes; irregular platelets, or rodlets. The outside surface of chopped wheat-straw is shown in a SEM image, (Figure 2.4-7). The size-reduction process introduces cracks and opens the straw structure. At higher magnification a possible wax pattern can be observed as crosses on the outside of the straw. The inside of the straw consists of small circular cells similar to a honeycomb structure (Figure 2.4-8).

Inglesby investigated unwashed stem and sheath of rice-straw and found a complex and heterogenic surface structure using SEM technique. The waxy layer and wax patterns on the straw surfaces could be observed for both extracted and non-extracted rice-straw samples. The estimation of the total wax content was approximately 1% extracted by hexane. Extraction by using a more polar liquid, ethanol-toluene azeotrope, yielded 3.1% of extracted materials (Inglesby et al., 2005).

2.4.2. Chemical composition of straw

Annual plant materials such as straw, bagasse and grasses are natural composite lignocellulosic materials mainly consisting of cellulose, hemicellulose, and lignin. Additionally, annual plant materials include a considerable amount of inorganic
components such as silicon, potassium, phosphorous, sodium, calcium, iron, aluminium and other elements of low concentration. The ash content is in the range of 4 – 20% and most of the ash consists of silica SiO$_2$.

Figure 2.4-7  SEM micrograph of the outside of wheat-straw (surface).

Figure 2.4-8  SEM micrograph of the inside of wheat-straw (surface).
The silica content of the ash in annual plants is approximately 40 – 75% depending on type of plant and preparation. The properties of washed straw were investigated by Jenkins, (Jenkins et al., 1996) and it was observed a wide variation of elements in straw depending on washing (leaching). The ash content of straw, grass and wood is presented in Table 2.4-2.

Table 2.4-2
Ash compositions of selected herbaceous fuels and wood (Jenkins et al., 1996)

<table>
<thead>
<tr>
<th>Oxide (% Ash)</th>
<th>Rice straw</th>
<th>Wheat straw</th>
<th>Switch grass</th>
<th>Sugar Cane trash **</th>
<th>Bagasse</th>
<th>Douglas Fir Wood</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>74.31</td>
<td>35.84</td>
<td>65.18</td>
<td>57.38</td>
<td>46.61</td>
<td>12.26</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.40</td>
<td>2.46</td>
<td>4.51</td>
<td>17.69</td>
<td>2.83</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.02</td>
<td>0.15</td>
<td>0.24</td>
<td>2.63</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>FeO$_3$</td>
<td>0.73</td>
<td>0.97</td>
<td>2.03</td>
<td>14.14</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>1.61</td>
<td>4.66</td>
<td>5.60</td>
<td>13.05</td>
<td>4.47</td>
<td>37.08</td>
</tr>
<tr>
<td>MgO</td>
<td>1.89</td>
<td>2.51</td>
<td>3.00</td>
<td>4.30</td>
<td>3.33</td>
<td>5.86</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.85</td>
<td>10.50</td>
<td>0.58</td>
<td>0.27</td>
<td>0.79</td>
<td>3.16</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>11.30</td>
<td>18.40</td>
<td>11.60</td>
<td>13.39</td>
<td>4.15</td>
<td>17.00</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.84</td>
<td>5.46</td>
<td>0.44</td>
<td>7.31</td>
<td>2.08</td>
<td>11.20</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>2.65</td>
<td>1.47</td>
<td>4.50</td>
<td>2.27</td>
<td>2.72</td>
<td>1.86</td>
</tr>
<tr>
<td>Und*</td>
<td>3.40</td>
<td>17.58</td>
<td>2.32</td>
<td>0.29</td>
<td>1.39</td>
<td>4.43</td>
</tr>
<tr>
<td>Ash (% dry Fuel)</td>
<td>19.60</td>
<td>13.00</td>
<td>8.97</td>
<td>5.04</td>
<td>2.44</td>
<td>0.45</td>
</tr>
<tr>
<td>Cl (% dry fuel)</td>
<td>0.74</td>
<td>2.02</td>
<td>0.10</td>
<td>0.22</td>
<td>0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* Undetermined, may consist primarily of chlorine and carbonates.

** Tops and leaves. Blank indicate not analyzed.

The silica analysed in ash is in fact not crystalline in the plant itself, several studies have shown that the silica occurrence is in the amorphous form or opal SiO$_2$ – H$_2$O composition (Jones and Milne, 1963; Jones et al., 1963). The amorphous form of silica is known as phytoliths or microfossils and has special shapes and micro-sizes (Ball et al., 1998, 1999). Moreover, the silica is deposited in distinct types of cells in the outer part of straws and grasses (epidermis). Milowych reported a conical shape of wheat-straw phytoliths by SEM analysis in the size of approximately 15 μm (Milowych et al., 1996).
3. ADHESIVE AND BONDING

The main types of conventional synthetic adhesives applied in the production of MDF are water soluble and contain formaldehyde. Urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF), and phenol-formaldehyde (PF) resins are the most common types of commercial adhesives for the wood-composite industry (Pizzi, 1983). Moreover, the most common non-formaldehyde wood-based adhesive is the methylene diisocyanate diphenyl (MDI) resin. This is one exception from the water-based system. However, development of water soluble MDI (eMDI) has been applied successfully for MDF (Moriarty, 1999). The MDI resin is also free from formaldehyde, and added in lower levels 3 – 6% (Rosthauser et al., 1997).

3.1. Formaldehyde resin

The most prominent thermosetting adhesives for wood-based composites in the forest product industry are urea-formaldehyde resins and melamine-modified UF resins (MUF). The UF resins are referred to a class of thermosetting adhesives defined as amino resins (Pizzi, 1983). Other examples of formaldehyde resins for wood-composites are phenol-formaldehyde (PF), melamine-formaldehyde (MF), resorcinol-formaldehyde and mixtures of UF, UMF, and PF adhesives. Depending on the amount of melamine in UF resin different nomenclatures of melamine-modified (or fortified) UF resins are current. For MUF resin containing less than roughly 10% of melamine the abbreviation UMF is commonly used by resin suppliers. In this thesis the MUF abbreviation is used for the whole range of melamine contents. Several advantages of UF and MUF resins for wood-based products are noticeable. Low cost, low cure temperatures, water or partly water solubility, resistance to microorganisms, excellent hardness, lack of colour, and resistance to abrasion are some of the good quality properties. However, the formaldehyde resin has the ability to release formaldehyde even after the curing. The emission of formaldehyde from urea-formaldehyde resins and MDF has been of major concerns and been argued for several years (Baumann et al., 2000; Sharp, 2004; Roffael et al., 2007).

In the MDF-process the UF resin is supplied as a linear or branched oligomer in an aqueous solution or partly dispersed solution. The UF-resin is added to the fibre and during heating (curing) in the hot-press a three dimensional polymer network is formed of the UF oligomers. Additionally, the cross-linked UF polymer is insoluble in water and other solvents. Before the addition of the UF resin into the MDF process a hardener (latent curing agent) is mixed into the UF resin as a catalyst, often a salt based on ammonium, e.g. ammonium chloride or ammonium...
sulphate. The properties and curing of melamine-modified UF resin is very depending on the process conditions, raw materials, methods of resin application, resin storage temperature, and resin storage time. The resin supplier is often forced to tailor-made the adhesive for optimal MDF-properties for each customer.

3.2. MDI resin

MDI used in straw MDF and straw PB has perhaps showed the most promising MDF panel properties. The general view of using MDI is excellent mechanical board properties, lower levels of consumed resin, but perhaps at slightly higher resin cost compared with UF resins. Moreover an elevated demand of formaldehyde free or low-emission adhesives in buildings, furniture and laminate fibreboard products have resulted in an increased market share. Formaldehyde emissions in full-scale production units will almost be eliminated if adhesives such as MDI are used. However, a small amount of formaldehyde will still be generated from the wood itself during the defibration process.

In general, a troublesome adhesion between the MDI resinated fibres and press plates and other metal surfaces has been reported (Pizzi, 1983). The pressing of wood-based MDF on an industrial basis is performed in a continuous process, in which the MDI resinated fibres are in direct contact with a hot steel belt during pressing. It is necessary to reduce the strong adhesion of MDI to the steel belt to avoid costly interruptions of operation and damage of press steel belts. Press-release chemicals are sprayed on the press steel belt or on the fibre mat feeding into the press. Alternatively, use of intermediate paper sheets to avoid direct contact with the MDI resinated fibres and the steel belt is also a possibility. The usage of press-release agents is necessary for the successful production of MDI-resinated straw-based fibreboards.

3.3. Non resin

Several investigations of non-resin fibreboards and MDF have been reported (Suzuki et al., 1998; Angles et al., 1999; Widsten, 2002; Velasquez et al., 2003a; Velasquez et al., 2003b). The main principle is to activate the outer surface layer of the fibre before pressing and create chemical bonding between adjacent fibres during hot-pressing. These ideas are connected to the non-resin fibreboards products in the mid 1920’s when full-scale production of wood fibres was possible by the steam gun principle (Mason, 1927). The MDF dry process generates a lignin rich fibre surface as a result of thermo-mechanical refining. It has been reported that the lignin can be activated by chemicals and enzymatic means to give lignin bonding functionality (Widsten et al., 2002; Felby et al., 2004; Widsten et al., 2004). The subsequently hot-pressing of fibres is said to be glued together by a self-
bonding adhesive. The concept for binderless straw MDF and the absence of a formaldehyde resin was believed to eliminate the formaldehyde emission and result in a minimal production cost. The bonding of the MDF is created by activation of the fibre surface by an oxidative treatment of the straw during defibration. The oxidative-activated fibre surface and low molecular degradation components are thought to create chemical bonds between activated fibre surfaces during hot-pressing. Fenton’s reagent (ferrous chloride and hydrogen peroxide) was the oxidative chemicals introduced into the defibration process to decompose the added hydrogen peroxide and form the intra- and inter-fibre interactions in the fibreboards (Widsten and Laine, 2004).

3.4. Bonding in MDF

In MDF the fibres are compressed and believed to be held together by hydrogen bonding and by a synthetic adhesive i.e. UF, MUF, PF, or MDI resin. Most of the adhesive is distributed on the fibre surface but a fraction of the adhesive penetrates into the porous cell wall through large pores, cracks, cavities and openings in the fibre. The link between fibre and resin in most cases is perhaps not of a chemical covalent-bonding character. Several theories of adhesion have been suggested (Pizzi, 1994). One of the probable adhesion theories of the UF resin bonding is believed to be physically and the UF resin is anchored into the cell wall structure of the fibre (mechanical entanglement/interlocking theory). During hot-pressing the UF resin forms bridges between adjacent resinated fibres and set the final structure of the fibre composite. The exact nature of the bonding mechanism of MDI resin has a more complex history and considerable controversy has been reported (Rosthauser et al., 1997). However, the adhesive bonding is strong and most of fractures recognized in the MDF failures were observed in the secondary wall at the S1/S2 interface within the cell-walls of the fibre and not in the adhesive (Butterfield et al., 1992).

4. THE MDF PROCESS

The dry-fibreboard MDF-process is mainly designed for wood-based materials. Softwood species are perhaps the most preferable raw material in the MDF industry. Hardwood species and mixtures of wood raw materials are common. Examples of hardwood are beech, eucalyptus, rubber wood, birch, and aspen. The variations of wood-materials for production of MDF are probably wider than for the pulp and paper industry. Small diameter tree and waste materials from saw mills can be used. The usage of urban-wood (waste wood materials from the building sector) and saw dust may also be applicable as raw materials for the MDF-industry. The basic principle of processing wood to MDF products imply a
thermo-mechanical process to convert solid wood material to separate fibres or fibre bundles, followed by the addition of adhesive for gluing fibres together and to compress the wood-based composite materials during hot-pressing to panels of various thickness and density. Figure 4.-1 shows a schematic drawing of the dry forming MDF-process.

Figure 4.-1 Process operations in the manufacture of wood-based MDF in the dry-forming method, permission of Metso.

4.1. Wood-based dry forming MDF process

The first steps in the wood-based MDF process are, debarking, size-reduction (chipping), screening, and washing of the raw material to get a clean and suitable size of the chips. An effective processing of wood to uniform and clean chips is essential to get a homogenous flow of the raw material into the Defibrator™ system. The Defibrator™ system is pressurized by steam usually within the range of 0.7 – 1.0 MPa which corresponds to 170 – 190 °C, typical upper design criteria is 1.2 MPa. The wood chips are pre-heated by steam (steam bin or surge bin) and forced into a vertical preheater by a screw feeder (plug-screw) to overcome the high pressure in the pre-heater. To obtain low electrical energy consumption during defibration of wood-based raw materials the temperature should be above the wood softening temperature, the glass transition temperature (\(T_g\)). The target is
to soften up the wood material and generate single fibres and fibre bundles as the material passes through the Defibrator, see Figure 4.1-1.

Defibration occurs when the wood material passes between grooved discs, a stator and a rotating disc (rotor) at high rotation speed 1500 – 1800 rpm. The disc surfaces are designed to have special patterns (segments) consisting of bars and dams. The direct contact between wood and the segment is concentrated in the outer part of the discs in the grinding zone (clearance). Figure 4.1-2 shows the main parts of the Defibrator™ system. The elevated temperature, steam, repeated compressions and shearing effects of the bars on the wood material cause the lignin in the middle lamella between the fibres to soften and break, hopefully most of the wood fibres separates and generates almost whole single fibres (fibre bundles). The thermo-mechanical pulping process produces both bundles of fibres and individual fibre. Moreover, the thermo-mechanical process will attack hemicellulose and initiate degradation. Volatile materials released from the fibres are carried away with the steam and released later from the fibre in the dryer. The distance between the discs
can be adjusted and together with different process temperatures and the retention times in the Defibrator™ system various fibre qualities can be produced.

![Figure 4.1-2 Defibrator™ system components top view, permission of Metso.](image)

The defibration process (refining) produces, steam, fibres and fibre bundles which exit the main refiner case through the blow valve and into the blowline. The fibre is pushed forward due to the centrifugal forces inside the refining zone and the pressure drop over the refiner discs and the blow valve. The fibre velocity has been reported to be close to the sound velocity in the end of the blowline (Chapman, 1999; Hague et al., 1999). Contrary, to the mechanical pulping of paper little interest is focused on breaking the fibre cell wall that cause fibres to become internally delaminated (fibrillated). Instead the created fibre surfaces in the MDF process are expected to be covered with lignin and to be compatible with added resin. The concept of liberating fibres from the wood matrix at different conditions is presented in Figure 4.1-3. The MDF-fibre is produced at high temperature and the fractures are located in the middle lamella due to the softening of lignin. The papermaking defibration (refining) process uses higher energy input at lower process temperatures and the applied energy fractures the wood eventually
resulting in fractures in the fibre cell walls. Lower temperature and higher energy input are necessary for paper quality fibres as compared to the MDF type of fibre.

Figure 4.1-3  Cross-section of fibres in the wood matrix displaying the basic fibre cell components. Different processing temperatures generate different types of fibre fracture and fibre quality.

Three fibre quality can be identified in Figure 4.1-3; (1) MDF-fibre (fibreboard), $T \gg T_g$. The middle lamella and defibrations temperature ($T$) is above the glass transition temperature ($T_g$). (2) Chemithermomechanical pulping, CTMP-fibre, $T \approx T_g$, fracture at the middle lamella and primary wall. Finally (3) Thermomechanical Pulping, TMP-fibre, $T \ll T_g$ failure at the secondary wall.

Defibration conditions at temperatures above 170 °C and MC of approximately 50% liberates extractives and low molecular weight components from the generated fibre pulp. Losses in TMP refining consist of fibre material dissolved or in a colloidal dispersion of hemicelluloses and degradation products. Amounts of 4 – 5% have been found typical for TMP from pulp mills in Finland (Holmbom et al., 2005). The hemicellulose carbohydrates may degrade and introduce carboxylic groups of the fibres (Roffael et al., 1994a, b; Lawther et al., 1995; Roffael et al., 1995; Lawther et al., 1996). The lignocellulosic materials are hydrolysed and converted into soluble sugars. A reduction of the fibre pH can be observed together with a yellowing of the pulp as the temperature and retention time in the defibrator.
system increases (Myers, 1987). Additionally, the lignin component situated on the fibre surfaces is important during hot-pressing. Fibre plasticization occurs and increases the interaction between fibres and improves MDF properties. Plastic flow of the surface lignin is depending on the water content and is most favourable at high pressure and temperature (Bouajila et al., 2005).

Figure 4.1-4 Resin penetration in a single fibre (Picea spp.) – Orthogonal cut view from ZEISS CLSM 3D projections. Green colour represents fibre and yellow colour represent added UF resin. (Cyr et al., 2008).

The addition of a synthetic adhesive (resin) is performed by introducing the adhesive into the blowline on wet hot fibres before the drying process or by addition of resin on dried fibres after the drying process. Adhesive and other additives may be applied by spraying resin on the dried fibres in separate blenders (drum-blending). The blowline resination is characterized by a high turbulence and effectively mixing of resin/fibres in the blowline. The resin is evenly distributed on the fibre surface and enables a good bonding between fibres. However, higher resin consumption has been observed in the blowline blending process compared with resin drum-blending of added resin to achieve desired MDF-properties. It has been speculated that the adhesive is pre-cured (adhesive consumed without contributing to bonding) at the extreme conditions in the blowline and dryer (Gran, 1982; Roffael et al., 2001; Cyr et al., 2008). The elevated temperatures in the blowline are much higher than the minimum cure temperature of a conventional UF resin (T > 65 °C). Fortunately, the retention time is very short and in the range of 3 – 8 s and the assumed pre-curing of UF resin is restricted. On the other hand mechanical blending of resin and dry fibre require complex spraying equipment and the resin spraying dyes in the drum-blender can be clogged up. Moreover, increased risk of resin spot on finished MDF is likely compared with blowline resination. It has also been reported penetration of UF resin into the fibre cell wall and lumen due to the low viscosity in the blowline.
resin blending. The penetrated part of the added resin will not contribute to effective bonding, thus higher consumption of UF resin is needed compared with other resin blending methods. An example of resin penetration of a fibre cross-section is shown in Figure 4.1-4.

The resinated fibre is dried in a flash tube drier to a MC in the range of 8 – 12%. The produced dry fibre mass is passed through a sifter to separate dense resin particles and similar defects from the fibres. The dry and resin coated fibres are then air-laid or mechanically distributed to a fibre mat for subsequent hot-pressing. The formed fibre mat is then compressed in a pre-press and trimmed by disc cutters before the finally hot-pressing and consolidation of the MDF.

4.2. Straw-based dry forming MDF process

The straw MDF process differs principally at the beginning of the MDF process as compared with the wood-based MDF. The difference is the dimensions of the raw materials. The straw length after harvesting is in the range of 0.3 – 0.5 m and the straw diameter is approximately 5 mm, depending on species. The wood-based raw materials are at least 10 times larger in size. Commercial production of straw MDF in full-scale mills does not exist today. Several attempts have been performed to produce straw panel boards and examples of particle board (PB) exist but not as conventional MDF where fibres are produced by pressurized defibration. One of the more famous examples is the strawboard manufacture at Isoboard (Williamson, 1997). Wheat-straw was the raw material and MDI resin was the applied adhesive. The Isoboard strawboard facilities was acquired by Dow BioProducts Ltd in 2001 and finally shut down in the year of 2006 due to low capacity. However, several pilot-plants for production of laboratory straw MDF are available; Bio Composite Center (Wales), Wilhelm-Klauditz-Institut, WKI (Germany), Washington State University, WSU (USA), and Alberta Research Council, ARC (Canada) are examples of institutes/universities equipped with necessary machines for production of MDF in pilot-scale.

Producing straw fibres in the pressurized Defibration™ system begins with a size-reduction process. Straw is cut (chopped) to a range of 10 – 50 mm in length for an effective internal transportation in screw conveyors and to get a proper straw bulk density. Moreover, the straw bulk density is an important parameter for the design and size of the equipment. The bulk density of straw is strongly dependent upon the type of handling and processing, example of different processes and bulk densities of wheat straw is showed in Table 4.2-1.
Table 4.2-1

*Densities of various storage forms of biomass*

<table>
<thead>
<tr>
<th>Wheat-Straw (Physical appearance)</th>
<th>Bulk Density (dry basis) [kg/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loose</td>
<td>20-40</td>
</tr>
<tr>
<td>Chopped</td>
<td>40-80</td>
</tr>
<tr>
<td>Bales</td>
<td>110-200</td>
</tr>
<tr>
<td>Moulded</td>
<td>96-128</td>
</tr>
<tr>
<td>Hammer milled</td>
<td>40-100</td>
</tr>
<tr>
<td>Cubed</td>
<td>320-640</td>
</tr>
<tr>
<td>Pelleted</td>
<td>560-720</td>
</tr>
</tbody>
</table>

It is observed that the bulk density of straw increases as the straw length is reduced (Lam *et al.*, 2008). The straw size-reduction methods generate also dust and small straw particles that can easily be removed by screening. The straw contains a high level of silicon and the silicon is concentrated to the outer straw surface layers (epidermis). It is desirable to remove dust and small particles by screening and de-dusting methods to avoid extreme levels of silica and ash contents in the finished straw MDF.

The size-reduced and dry straw material is later heated with steam and hot water in a screw mixer or soaked in water. It is also possible to add chemicals at this stage. The objective is to increase the moisture content and temperature and in some cases reduce the pH and the pH-buffering capacity of the straw material to achieve an optimal curing of the adhesive (UF resin) during the hot-pressing of straw MDF. Example of the different processing steps of the Defibrator™ system for straw preparation is shown in Figure 4.2-1. Some reports describe the possibility to add NaOH or alkaline salts for preparation of straw and removal of the surface wax (Mantanis and Berns, 2001). Straw that has been heated and moistened will initiate a softening of the material and loosen up the straw structure. The amorphous hemicellulose is partially hydrolyzed to mono- and oligosaccharides when acids are added. Moreover, a slight washing effect can be attained and the silicon, potassium, and calcium content are reduced (Jenkins *et al.*, 1996). Some of these materials can be squeezed out from the plug screw in the Defibrator™ system in a side stream of contaminated water. The pre-treated straw material is thereafter fed into a horizontal pre-heater (digester) and defibrated in a pressurized single-disk refiner.
In the Metso Technical Center pilot-plant in Sundsvall, Sweden a Defibrator™ system of type OHP 20 with a plate diameter of 508 mm (20 inches) has been used for straw fibre production. Refining was done at a rotational speed of 1500 rpm and the target pressure were in most cases slightly lower than for wood-based MDF defibration and in the range of 0.5 – 0.7 MPa. The pre-heating retention time in the Defibrator™ system has been in the range of 1 – 3 min. The refined fibres are discharged from the refiner housing into a blowline and mixed with an adequate resin. The resinated fibres are dried in a continuous flash dryer connected to the blow line. The average dry content of dried resinated fibres is approximately 90%.
5. THE MDF PRODUCT

MDF has enjoyed success in the fibreboard industry for many years. The furniture industry in general, laminated floor products, doors, wall panelling, window boards, sculptures, loudspeakers and hi-fi equipment, musical instruments, toys, garden furniture, and similar interior and external building products are example of existing markets. The properties of finished MDF are regulated in several types of standards. In this thesis the requirements of MDF-properties in dry-conditions are applied (EN 622-5, 2006). For rice-straw MDF the properties were evaluated according to (American National Standards Institute (ANSI), 2002).

5.1. MDF vertical density profile

Wood-based composite panels or MDF usually require a vertical density profile (VDP). In Figure 5.1-1 a typical VDP is displayed and characterised by a high surface density 900 – 1100 kg/m³ and a core density in the range of 650 – 800 kg/m³.

![Figure 5.1-1](image)

Figure 5.1-1 Vertical density profile of a typical hot-pressed wheat-straw MDF panel. The average calculated core density is represented by a horizontal dotted line (---).

The VDP is formed during the hot-pressing. The fibre mat is conveyed to the press where the densification begins with a hot compression of the fibre mat to high densities > 900 kg/m³ during a rather short press-cycle time of 10 – 20 s of the total press-cycle. The surface layers are immediately heated in contact with the hot press-platens and the thermo-setting adhesive is cured and fibres are glued.
The compression and heating of the resinated fibre create a high-density surface layer composed of flat fibres, see flat cross-section in Figure 5.1-2. The pressure is reduced and the gap in the hot-press is slightly expanded due to the spring-back (decompression) of the fibre in the core. Consequently, the density of the core component of the fibre mat decreases and the cross-section of fibres almost retain the original geometry. After a while heat is transferred into the core and cures the thermo-setting adhesive. Bonds between fibres at the core are created and fix the final dimension of the MDF Board. The average density of the finished board is usually in the range of 700 – 900 kg/m³. When the press-platens are opened the finished MDF board will have a variation in density in the thickness direction, and a vertical density profile is formed. Flat cross-sections of straw fibre have been reported for a straw/polyester composite application (White and Ansell, 1983). The dry fibre was crushed during compression and the strength of the fibre was calculated. In hot-pressing of MDF fibre the higher moisture content and heat in the surface layer improve the flexibility of the lignocelluloses, resulting in less crushing of fibres.

![Figure 5.1-2 Cross-section of partially crushed straw fibre (White and Ansell, 1983).](image)

The VDP of the MDF have several benefits, the hard (high density) surfaces are suitable for laminating, bending properties are optimized and the dimensional stability due to swelling is improved. Several reports also discuss the influence of average density, core density and surface density of various MDF-properties (Xu and Suchsland, 1998; Xu, 1999).
5.2. MDF properties and requirements

The strength and physical properties of wood MDF material composites are closely related to the MDF density and the resin content. Increased density and resin content improve the mechanical and physical properties of fibreboards (Suzuki and Kato, 1989). However, improved properties by addition of more adhesive or wood materials (increased density) are generally connected to increased cost of the MDF. The extra addition of adhesives or wood does not generate an increased volume of MDF Board.

The MDF panel product is produced in several thicknesses between 3 to 40 mm and in most cases the densities increases as the thickness is lowered. The typical MDF properties measured are Internal Bond (IB), Modulus of Rupture (MOR), Modulus of Elasticity (MOE), Thickness Swelling (TS) and Water Absorption (WABS). Other important properties of the MDF as screw holding and formaldehyde content (perforator value) but will not be discussed here.

IB is the strength measured in the z-direction of the MDF and is a good indication of the bonding strength between fibres and the effectiveness of the adhesive. IB of MDF is typical in the range of 0.55 – 1.20 MPa. The bending properties MOR and MOE are important material properties of the wood composite MDF Panel. The MOR property reflects the amount of mass or force that the composite MDF Panel can bear, i.e. the bending (deflection) of a shelf. The MOR of MDF is in the range of 20 – 40 MPa. MOE is the corresponding material constant and exhibit values in the range of 2.5 – 4.0 GPa. The water absorption and the thickness swell of MDF are measured by water soaking during 24 h exposure. This is the primary measurement of the water resistance of the MDF. The range of the TS of wood-based MDF is in the range of 5 – 30%, dependent on the panel thickness there are different swelling requirements defined. Water absorption is the measurement of the corresponding water weight increase.

Fibre density is a profound variable that affects most of the fibreboard properties and different correlations have been reported of fibre properties and MDF density (Suzuki and Kato, 1989; Okuda and Sato, 2004; Lee et al., 2006). Furthermore, a study of steam-pressed MDF (MDF consisting of a uniform density profile) shows interesting relations between average density, internal bond and thickness swelling (Figure 5.2-1). In general the TS and IB are improved as the density increase.
5.3. Economical and environmental aspects of straw MDF manufacture

The specific selection of straw and agriculture wastes as a raw material for refinement of biomass depends on a variety of factors. The most frequent factors mentioned for conversion of straw to bio-ethanol, bio energy and composite boards are based on availability, quality, quantity, removal, transportation, storage, and landowner/producers costs (Nielsen, 1995; Kerstetter and Lyons, 2001). The main environmental benefits are the reduced open field burning of an annual plant and to capture carbon dioxide (CO$_2$), the biological sink for extended time into MDF panels, instead of converting straw directly into bio energy or applying straw fibre a few times as recycled paper. Additionally, the straw MDF panels can be recycled or converted to energy after utilization. There are two types of straw fibre resources for industrial applications grown in large areas of the world; wheat and rice-straw. The MDF process has essential advantages since it can produce fibreboard from readily available and renewable raw materials. Most of the straw plant can be converted to fibreboard products and the rejected materials can be integrated in the energy system of the MDF mill. The reject from

Figure 5.2-1 Thickness swelling of MDF samples of uniform density profile as a function of IB and density. Permission of Göran Lundgren and Kurt Schedin.
the energy generating system or ash is potentially a substance that can be returned to the farmer and regain essential mineral components to the ecosystem. In the production of bio energy and also the production of paper products the high silicon and ash content of rice-straw is a profound disadvantage. The silicon in combination with other inorganic components will build up in the chemical recovery system of the pulping process and require special care and extra costs. In bio-energy applications the high ash and silicon content of rice-straw complicate the burning technique and handling of large amounts of ash. Wheat-straw and rice-straw are therefore promising candidates for the manufacture of MDF.

The wood-based MDF industry can today offer MDF panels with enhanced moisture resistance, improved flame retardance properties, reduced formaldehyde release or formaldehyde-free adhesives. The development of high-performance straw MDF requires similar properties and several conventional binders (adhesives) must be tested and verified for straw-based MDF. The processing conditions between wood and straw-based raw materials differ and different adhesive system can perform in unexpected ways for different types of raw materials. The most common adhesive systems used today are based on formaldehyde, UF, MUF, and PF. Together with a formaldehyde-free resin as MDI a need for evaluating different types of adhesives for straw MDF is in progress.

6. MATERIAL AND METHODS

This section briefly describes the materials and methods used in Paper I-IV. In section 6.1 the raw materials, experimental methods, and measurements of straw material are presented. The measurements of pH, pH-buffering capacity, and other fibre pulp properties performed in an optical laser instrument PQM 1000 of refined fibre are described in section 6.2. The methods and measurements of straw MDF properties are presented in section 6.3.

6.1 Raw materials

6.1.1. Wheat-straw substrate

In the first investigation (Paper I) wheat-straw (Triticum aestivum L.) was taken from north-eastern China. The wheat-straw (WS) was harvested in different seasons, and some of the wheat-straw was stored in dry conditions for 1 year. The dry content of the delivered straw was approximately 90%.

The wheat-straw (Triticum aestivium L.) used for the non-resin fibreboards was grown and harvested in Uppsala province, Sweden (Paper II and IV). The wheat-
straw (WS) was cut to about 30 – 40 cm in length, dried in the field, and finally baled. The moisture content of the baled WS was approximately 15%.

6.1.2. **Rice-straw substrate**

Rice-straw (*Oryzae Sativa* L.) was harvested; baled; and stored in California, US, Willows (Paper III). The moisture content of the baled straw was approximately 15%. The dried and baled rice-straw was cleaned; chopped; and hammer-milled before transportation to Metso Paper Technology Center in Sundsvall, Sweden, where the defibration and production of rice-straw fibres were performed.

6.1.3. **MUF resins and chemicals for the production of wheat-straw MDF**

The adhesives and chemicals used in the manufacture of straw MDF have been of different types and adapted to the straw substrates. For the wheat-straw MDF (Paper I and Paper IV) two types of commercial melamine-modified Urea Formaldehyde (MUF) resins were used. The MUF resins were supplied by Dynea NV (Prefere 11G321) and Akzo Nobel Casco Adhesives AB (UMPF 1074-0837). The latter MUF resin contained approximately 30% melamine and a minor amount of phenol. Some of the UF resins were mixed to reduce the melamine content to an estimated 20%. An aqueous solution of ammonium chloride was added to the MUF resins as a hardener (1.0%) and hexamethylenetetramine (0.2%) was added as a retarder. Both the commercial MUF resins and the mixed resin mixture were finally diluted to 50% before application. The target content of the MUF resin ranged from 14 to 19% in relation to the dry wheat-straw (dry basis, d.b.). A small amount of wax is usually added to the fibre flow to improve the water resistance of the finished wood-based MDF panels. In this study, the wax was injected at the infeed of the refining process. The wax emulsion was supplied by Emutech AB, Sweden, Boardwax B100 and was diluted to a solid content of 30% before use. The target level of wax emulsion was 1.0% (d.b.) in relation to the wheat-straw.

6.1.4. **Chemicals for the production of non-resin wheat-straw MDF**

The experiments were carried out using hydrogen peroxide of pure grade (Labservice, Sundsvall, Sweden) supplied at a concentration of 35%. The hydrogen peroxide was diluted and added to the blowline to react with and activate the fibre surface. The hydrogen peroxide reaction was catalyzed by metal ions and ferrous sulphate (FeSO₄·7H₂O) of pro-analysis grade (Labservice, Sundsvall, Sweden). The size-reduced wheat-straw was pre-treated before defibration by introduction of an acid. Diluted sulphuric acid (10%) of analysis grade (Labservice, Sundsvall, Sweden) was added to the hot water, steam, and wheat-straw. An aqueous solution of calcium chloride, CaCl₂·6H₂O, pro-analysis grade (Labservice,
Sundsvall, Sweden), was added to decrease the hydrophilicity of the fibre surfaces and to improve the water-repellent properties of the finished fibreboards.

6.1.5. MDI resin and chemicals for the production of rice-straw MDF

A commercial methylene diphenyl diisocyanate (MDI) resin was supplied from Huntsman (Rubinate 1840). The addition of MDI resin was set to 3, 4, and 5%, on a dry fibre basis. A wax emulsion from Borden (Cascowax EW-58A) was added at a level of 1%, on a dry fibre basis. The investigated press-release agent (Chemrelease RCTW-9495) was supplied by Chem-Trend L.P., Howell, MI.

6.2. Preparation of straw substrate

The manufacturing of MDF based on different species of straw includes several process steps, see Table 6.2-1. The straw fibreboard processing is similar to the wood-based MDF/HDF dry process. However, the main difference in the manufacturing of straw MDF as compared to wood-based MDF is the preparation of the straw-based materials before refining.

Table 6.2-1

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Wheat-straw</th>
<th>Rice-straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Size reduction and screening</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Wetting (Soaking)</td>
<td>Wetting, acid</td>
<td>Soaking</td>
</tr>
<tr>
<td>3</td>
<td>Defibration</td>
<td>7 bar, 3 min</td>
<td>6 bar, 1 min</td>
</tr>
<tr>
<td>4</td>
<td>Resination</td>
<td>Blowline-blending</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Adhesive (Resin)</td>
<td>UF, MUF, MUPF, (H₂O₂)</td>
<td>Resin-blender MDI</td>
</tr>
<tr>
<td>5</td>
<td>Mat forming</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pre-pressing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Hot-pressing</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Debaling, chopping to suitable straw lengths, dusting, cleaning, and wetting of the straw are new components in the straw MDF process. Furthermore, the generated straw dust and small particles in the preparation process are removed for a better adhesive efficiency, also resulting in reduced silica content in the finished straw MDF.
6.2.1. Size-reduction of the straw material

Wheat-straw was hammer-milled to reduce the size of the straw length after debaling. The first hammer-mill was a Jeffery Swing-hammer Shredder, 15 inches × 8 inches, and installed with 25 mm screens. The second hammer-mill, model H-30.C (Kamas Industri AB, Karlstad, Sweden), was equipped with oval screening holes with 10 mm aperture. The rotation speed of the first hammer-mill was 1000 rpm and of the second was 1500 rpm. A production rate of 60 kg/h was selected. The resulting straw length of the feedstock was approximately 10 – 15 mm. The straw material was sieved in typical screening equipment using a 0.7 mm mesh.

An alternative method for raw straw size-reduction was performed for the wheat-straw used in the production of non-resin straw MDF. The full-length straw material was chopped to a length of 25 – 50 mm. Subsequently the chopped straw was subjected to a low-energy hammer-mill and screening process to remove dust, straw fragments, and straw particles. The hammer milling and de-dusting were conducted at the Förderanlagen Gmbh KG (FMW) facility in Kirchstetten, Austria.

6.2.2. Pre-treatment of straw

The size-reduced straw materials were pre-treated with steam, hot water (60 °C), and/or acid added to a mixer screw to increase the temperature of the size-reduced straw to approximately 80 – 90 °C. The dry content of the wheat-straw after pretreatment was approximately 50%. Sulphuric acid solution was introduced to the straw material in some of the trials. For the production of non-resin MDF sulphuric acid was added to reach a target level of 0.75% (dry basis) based on dry wheat-straw. The moisture content (MC) was increased and the pH of the wheat-straw mixture was decreased to approximately 4 – 5 pH-units. The production rate was approximately 120 kg/h. A slightly higher MC level of the pre-treated wheat-straw was obtained (MC = 107%). In the production of the rice-straw MDF another wetting method was applied. The rice-straw was soaked in water for 24 h before defibration.

6.3. Defibration of straw

The pre-treated wheat-straw was fed into a horizontal pre-heater (digester) and defibrated in a pressurized single-disk defibrator, type OHP 20 laboratory Defibrator™ system (Metso Panelboard, Sundsvall, Sweden) with a plate diameter of 508 mm (20 inches). Defibration was done at a rotational speed of 1500 rpm for all investigated raw materials. Wheat-straw was refined at pressure of 0.6 – 07 MPa. The retention time in the Defibrator™ system was set to 1 – 3 min. Rice-straw was refined at a slightly lower pressure and retention time, approximately 0.6 MPa and 1 min. The defibrated fibres were discharged from the refining house into a
blowline and mixed with thermosetting adhesives. The resinated fibres in the blowline were dried in a connected continuous flash dryer. The average dry content of dried defibrated fibres was approximately 90%. The rice straw fibre was resinated in a resin drum-blender and mixed with MDI resin after the fibre drying operation.

6.4. Fibre forming and pre-pressing

Resinated dry wheat-straw fibres were formed batch wise in a 500 × 600 mm² forming box Pendistor™, (Metso, Sundsvall, Sweden). Depending on the target densities and the thickness of straw MDF-panels, different fibre weights were selected. Finally, the fibre mats were pre-pressed in a cold daylight press at 1.0 MPa for 60 seconds. For rice straw the same fibre forming principal was applied and the fibre was manually formed and pre-pressed.

6.5. Pressing of MDF

The pressing cycle was guided by in-house experience of pressing annual plant fibre materials. The overall goal was to press panels for a time of 12 – 13 s per millimetre of the panel thickness. The total pressing times were 130 or 200 s, depending on the final panel thickness of 9 or 16 mm. The press-plates temperature was set to 190 °C and the resulting maximum temperature in the core of the fibre mat during pressing was approximately 105 – 110 °C.

One inconvenience when pressing straw fibre materials is the long de-gassing time necessary to release entrained steam and air to avoid delamination of pressed panels. To overcome this obstacle an extra feature was added to the press heating system. Oil at a temperature of 60 – 80 °C was circulated into the hot press plates for cooling. This was arranged in the end of the pressing to reduce the build-up of steam pressure inside the panel. The time for cooling was one third of the total pressing cycle. The applied pressure in the beginning of the pressing was set to 0.5 MPa during 10 – 15 s to create a high surface density of the panel. The pressure was then regulated to approximately 0.05 MPa for adjusting of the core density. Finally, the pressure was set to zero for opening of the press.

Rice straw fibre was pressed without cooling system and was pressed during longer times, approximately 20 mm/s, at thicknesses of 4 mm and at higher densities of the finished rice-straw MDF panels, see details (Halvarsson et al., 2010a).
6.6. Evaluation of straw fibre and medium density fibreboard

6.6.1. Straw fibre properties
Resinated and dried straw fibres were sampled after the dryer cyclone. The size and shape of fibres were measured by image analysis using a laser-based PQM 1000 pulp quality monitoring system (Metso, Sundsvall, Sweden).

6.6.2. Mechanical properties of straw MDF
Straw MDF panels were cut into 50 × 50 mm² pieces for determining of internal bond and for measuring density profiles. Bending strength, modulus of rupture (MOR) and modulus of elasticity were measured on 4 × 32 cm². The mechanical properties IB, MOR, and MOE, were determined according to the EN standard methods (EN 310, 1993; EN 319, 1993) in an Alvetron TC 10 testing instrument. The pressed panels were stored for one week at room temperature after pressing. Before testing, the specimens were conditioned in a room for 48 h at 65% relative humidity and a temperature of 20 °C. Rice straw MDF was tested according to (American Society for Testing Materials, 2006).

6.6.3. Resin content of straw MDF
The MUF resin content was analysed using the Kjeldhal method and the nitrogen content of the finished straw MDF panels was measured using the Kjeltec System 1026 Distilling Unit.

6.6.4. Thickness swelling and water adsorption of straw MDF
Thickness swelling (TS) and water adsorption (WABS) properties were determined according to the EN standard (EN 317, 1993) of 50 × 50 mm² pieces of straw MDF. The straw MDF specimens were immersed vertically in water for 24 h to determine thickness and weight. Rice straw MDF was tested according to (American Society for Testing Materials, 2006).

7. RESULTS AND DISCUSSION

This section presents the major results from the studies on the manufacture of wheat and rice-straw medium density fibreboard. The development and production of wheat-straw MDF and melamine-modified urea-formaldehyde resin in pilot plant scale is described in Paper I and IV. Production of rice-straw MDF and methylene diphenyl diisocyanate resin is reported in Paper III. The manufacture of non-resin (binderless) wheat-straw fibreboards is presented in Paper II.
7.1 Manufacture of wheat-straw MDF

In the past several attempts have been made to produce MDF based on straw and urea-formaldehyde UF resin. The manufacture of wheat-straw MDF and PB in combination with UF resin has resulted in acceptable mechanical board properties but still the thickness swelling and water resistance of UF straw particle boards have higher TS than wood-based board products (Sauter, 1996; Markessini et al., 1997; Han et al., 2001a; Wasyliciw, 2001; Mo et al., 2003). The poor to moderate thickness swelling properties of such straw boards are explained by insufficient wetting of straw material by UF resin. It is speculated that hydrophobic chemical components occurring naturally on external straw surfaces reduce wetting of water-based adhesives (Liu et al., 2004). However, increased melamine content in modified UF resin improves the water-repelling properties and improved MDF properties are achieved (Hervillard et al., 2007). Chemical modifications of straw and straw fibres by acetylation improve the TS. Very low thickness swelling of produced straw MDF less than 2% thickness swelling have been reported (Gomez-Bueso et al., 2000). The main chemical components of the external straw surface are wax, pectin, and silica (Wisniewska et al., 2003). Eventually, pressurized refining of wheat-straw under appropriate processing conditions disintegrates the straw material and generates fibre bundles and fibre of sufficient quality (Sauter, 1996). Separating most of the above-mentioned components from the produced fibre materials improves the wetting of water-based resins. Several basic parameters and methods for the reduction of water uptake and thickness swelling of wood-based MDF are available. In this investigation the strategy was to reduce the amount of small particles and dust from the straw; pre-treatment of size-reduced straw with hot water, steam, addition of acid; modify the UF resin by improved hydrophobic property by increased melamine content and/or by introduction of small amounts of phenol components. Finally, the trials were designed to produce straw fibre of sufficient quality for optimal bonding by variation of the refining conditions.

7.1.1 Size-reduction of wheat-straw

Straw was processed in a hammer-mill to reduce the size of the straw to achieve a proper straw-length and bulk-density for handling and transportation of the straw in the subsequent process. It was observed that large amounts of dust and small particles were generated in the hammer-milling process. The basic structure of straw contains less fibre material and more potential rejects than typical wood-based raw materials. Consequently, the first parameter for improving mechanical properties and TS of straw MDF was to reduce the amount of small particles and dust through out the entire process. The defibration of straw will also generate additional small fragments and dust when producing fibre. Unfortunately, higher amount of dust and particles in the straw MDF process require more adhesive to reach the same mechanical properties and water resistance as wood-based MDF.
The bonding in MDF is less effective when increased amounts of particles, straw fragments, and dust are present in the produced MDF fibre and in the finished MDF panels.

The wheat-straw was size-reduced to a length of 10 – 25 mm and the straw bulk density was within the range of 60 – 100 kg/m$^3$. A sample of unscreened size-reduced wheat-straw was fractionated to measure weight, ash content, and the level of silicon in the different straw fractions. Silica, sand, and inorganic compounds are also undesired components in the MDF process, as they can cause increased tool wear. Effective screening of the size-reduced straw is an appropriate way to improve the MDF properties. The dry screening of a typical size-reduced wheat-straw quality was performed in a screening apparatus (Allgaier-Werke) equipped with three screens. The screen-opening diameter and yield for each fraction are summarized in Table 7.1-1. Straw thickness rather than length was the significant property for separation in this type of screening process. The size-reduced straw material, passed through screen openings of 1.0 mm or smaller. Approximately 77% of the material remained on the first screen, followed by 10% each on 0.6 and 0.2 mm screens. Finally, the smallest particles, straw fragments, and dust were captured as Fraction D (PAN); the PAN or straw particles < 0.2 mm comprised approximately 3% of the total amount of the straw material.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Screen-opening Diameter [mm]</th>
<th>Wheat-straw yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction A</td>
<td>&gt;1.0 mm</td>
<td>76.8</td>
</tr>
<tr>
<td>Fraction B</td>
<td>&gt;0.6 mm</td>
<td>10.0</td>
</tr>
<tr>
<td>Fraction C</td>
<td>&gt;0.2 mm</td>
<td>10.0</td>
</tr>
<tr>
<td>Fraction D (PAN)</td>
<td>&lt;0.2 mm</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 7.1-1
Fractions and Yields of Size-Reduced Wheat-straw; Percent Weight Left on the Specific Test Screen

7.1.1. Ash content of wheat-straw fractions
The ash content of the wheat-straw fractions was in the range of 6.5 – 14.7%, the maximum ash content being observed in Fraction D (Figure 7.1-1). The original hammer-milled wheat-straw sample had an ash content of 7.2%.
Agricultural wastes and wheat-straw have much higher ash contents than do wood-based materials (Jenkins et al., 1996). In general, the ash contents of straw materials are in the 4 – 19% range, silica and potassium oxide being the dominant components. The recommended silica content (sand content) in ash from wood-based MDF is 0.05%. Deposits of microfossils or phytoliths in straw plants explain the high ash and silicon content of the wheat-straw.

Figure 7.1-1  Ash content of size-reduced wheat-straw and of four screened wheat-straw fractions. Numbers below each fraction indicate the screen opening in mm.
7.1.2. Elemental analysis of ash from wheat-straw and straw fractions

The chemical composition of wheat-straw surface layers has been analysed using Fourier transform infrared spectroscopy (FTIR). It was reported a high level of silicon in the surface layer (epidermis) (Milowych et al., 1996; Yao et al., 2003). In the present investigation, ash originating from the screened fractions of wheat-straw was subjected to elemental analysis using EDX methodology. The silicon weight fraction of the ash samples increased as the particle size decreased (Figure 7.1-2). The silicon content from the original size-reduced wheat-straw ash sample was nearly 12%. The silicon content of ash samples of Fractions C and D displayed the highest values and exceeded 17%. The strengthening and protective parts of the wheat-straw are located on the outer part of the straw (Liu et al., 2004). Hammer-milling and intensively processing of the dry brittle straw components degrades and crushes tissues and cells on the straw surface. Consequently, most of the silicon found in straw is expected to be situated on the external surface parts of the internodes. Small particles, fragments, and dust are easily removed from the straw and are found in the fine particle fractions.

Figure 7.1-2  Silicon content (%) of size-reduced wheat-straw and of four wheat-straw fractions after screening and ashing. Numbers below each fraction indicate the screen opening in mm.
7.1.3. The pH and buffering capacity of wheat-straw and wheat-straw fractions

The curing reaction of UF resin is initiated by heat and accelerated by slightly acid conditions. The curing rate of UF resin when pressing wood-based fibre material is generally not a problem in conventional MDF manufacture (Xing et al., 2006). The typical pH of refined wood-based fibre is below 6 and typical having pH values in the 3.5 – 5.5 range. Unlike wood materials, wheat-straw and cereal wastes have higher pH values and pH-buffering capacity levels, pH-levels above 7 are not being uncommon. Generally, the curing rate of UF resins is reduced at pH between 6 and 8 or in combination with a high pH-buffering capacity. In some investigations the poor properties of straw MDF have been associated with an unfavourable pH and pH-buffering capacity of the refined straw fibre.

The wheat-straw was analyzed with respect to pH and pH-buffering capacity. In a study of Swedish wheat-straw the pH was in the range of 7 – 8. The pH-buffering capacity was analyzed for both acid treated and untreated size-reduced wheat-straw. The pH-buffering capacity of the untreated wheat-straw particles was close to a level of 27 mL but was reduced to around 22 mL after the acid treatment (Figure 7.1-3).

![Figure 7.1-3](image-url)  The pH buffering capacity of Swedish wheat-straw after pre-treatment with acid or only water.

Figure 7.1-4 shows the pH variation of the four wheat-straw fractions (see chapter 7.1.1) as a function of added acid. The initial pH of all fractions was approximately 7.5 and declined after the addition of acid. Fraction A (wheat-straw particles left on
1.0-mm screen openings) needed the least addition of acid, only 12 mL, to reduce the pH to 3.0. Fraction D (the fine wheat-straw particles below 0.2 mm in size) displayed the highest buffering capacity, and 15 mL requiring of acid solution to reach pH = 3.0.

![Figure 7.1-4 pH and pH-buffering capacity of four wheat-straw fractions.](image)

Silicon and other chemical components are concentrated in the fine particle fraction and most likely contribute to the increased buffering capacity. Considering the optimum conditions for the UF resin curing reaction, it is important to remove inorganic compounds from the fine fractions to enhance and maintain curing at the same level as in MDF panel production from wood-based materials. The pH buffering chemicals left on the straw after size-reduction and screening can be neutralized by addition of a small amount of acid in the pre-treatment process.

### 7.1.4. Pre-treatment of wheat-straw and effect on the straw fibre

The addition of hot water (steam) to the straw in the pre-treatment operation increases the moisture content of straw from approximately 10 to 100% (d.b.) (50% dry content). Most of the water is adsorb on the straw surface and a part of the water and chemicals can be squeezed out from the straw at the infeed screw before the refining process. The hot-water, steam, and acid pre-treatment before refining is performed to increase the temperature, soften up the straw material, and reduce friction in the infeed system to the Defibrator™ system. The acid is added to reduce the pH for improving the curing rate of added UF resin. Generally, a reduction of pH is obtained of wood furnishes without addition of acid during
pressurized defibration. Several degradation processes of the lignocellulosic during defibration at high temperatures, approximately \( T > 150 \, ^\circ\text{C} \) initiate formation of acidic components and discolor the fibre due to a presumed formation of carboxylic groups (see chapter 4.1). The retention time in the digester (pre-heater) will also influence the pH of the defibrated lignocellulosic fibre. Although, acidic conditions are important for optimal curing of the UF resin, the resin itself is slightly alkaline. Addition of large amounts of UF resin > 13\% (d.b.) contribute to a small increase of the pH of the resinated straw fibre. Pre-treatment of straw without acid can display a level of 6 – 7 of resinated straw fibre. The pH of resinated straw fibre will be influenced of the raw material used, the specific processing conditions during the defibration process, additives, resin content, and type of urea-formaldehyde resin.

Defibrated wheat-straw fibre showed a lower pH and lower pH-buffering capacity compared with the original wheat-straw. The curing reaction of UF resin is catalysed by hydrogen ions, and for some straw qualities acidic impregnation or pre-treatment of size-reduced straw can be advantageous. In most cases the pH of straw furnish is higher than in wood. The pre-treatment of straw by addition of acid can be a way to level out large pH-variations and get a better control of the raw-material and process.

7.1.5. Defibration of wheat-straw

The structure and composition of wheat-straw differ from wood furnish. The fibre length of wheat-straw under optimised process conditions is in the range of 0.9 – 1.4 mm (Jacobs et al., 1998; Rowell et al., 2000). The average straw fibre length for MDF is shorter than fibre produced of conifers and most deciduous trees. The defibration conditions are rather different from the typical conditions selected when refining wood. Investigations of process conditions during pressure refining of wheat straw have been reported (Sauter, 1996; Eroglu and Istek, 2000; Han et al., 2001b; Wasylycwiw, 2001). The typical refining conditions of wheat-straw is in the range of 0.6 – 0.7 MPa steam pressure and 60 – 120 s retention time. Moreover, the thermo-mechanical processing of straw produces more small particles, fragments and dust than refining of wood-based materials. In this investigation dust is defined as straw fragments and dust less than 0.45 mm. The selected process parameters are balanced between producing an optimal fibre length and minimizing the amount of dust to achieve acceptable MDF properties. Defibration performed at 0.6 MPa and 2 min. retention time indicated wheat-straw fibre of sufficient fibre quality. In general, defibration of wood-based materials require higher temperature (steam pressure > 0.7 MPa) levels and longer retention time (> 3 min.) to get the suitable fibre quality for production of wood-based MDF panels.
The fibre length distribution of wheat-straw fibre samples was analyzed in the PQM 1000 system. Length distribution curves of a typical Swedish wheat-straw fibre samples followed together as a function of the fibre length (Figure 7.1-5). The plotted curves are independent of resin type, resin content or other fibre treatments. Moreover, a typical MDF fibre sample of refined Scandinavian pine has been plotted as a reference in Figure 7.1-5.

Figure 7.1-5  PQM 1000 fibre length distribution. Fibre weight distribution vs. fibre length. (WS in the legend represent wheat-straw, UF urea formaldehyde, and UMF urea melamine formaldehyde.

The average fibre length of wheat-straw fibres is calculated to an average value in the range of 0.9 – 1.0 mm which is shorter than the fibre length of wood; it is observed that wood fibre is approximately twice the average fibre length of straw fibre. Additionally, wheat-straw generates larger amounts of short fibre and dust compared with a pine furnish. The amount of fragments of straw fibre and straw particles less than 0.45 mm was more than twice the amount of pine fibre. Furthermore, detailed conditions of the straw process are described in (Halvarsson et al., 2008). Synthetic resin is injected in the blowline. Wax was added into the defibrator infeed screw. The fibre-resin-wax mixture is then flash dried to a dry content of 88 – 92% and the UF resin will cover the straw fibre surface but is not cured.
7.1.6. Pressing and properties of wheat-straw MDF

The MDF samples in this examination were comprised entirely of wheat-straw and UF and UMF resins. Before pressing, the wheat-straw fibre was formed into a rectangular fibre mat sized in dimension adapted to the hot-press plates. Depending on the density of finished MDF the height of the fibre mat differ. The prepared fibre mats were pre-pressed in a cold press to reduce the fibre mat height and make a homogenous fibre mat. The fibre mat was then placed into the hot-press and compressed into its final thickness. The pressure, pressing time, and generated heat create fibre bonding and consolidate the straw and UF resin into MDF. Depending on selected press parameters different thickness and densities of the MDF are produced. The pressing of MDF will also generate a vertical density profile. The unique possibility to cool the hot press-plates at the end of the press-cycle reduces the risk for delamination of the fibreboard and improves the possibility for control of the VDP.

![Figure 7.1-6 Internal bond (IB) of wheat straw MDF vs. core density at different resin contents (RC).](image)

The IB strength of wheat-straw MDF is strongly depending on density. Increased average density or core density improves the mechanical properties. IB as function of core density is presented in Figure 7.1-6. Straw MDF was produced at different resin contents. The most challenging property of straw-based MDF is the moderate water resistance. In general the mechanical properties of straw MDF panels display appropriate strength levels. The main effort to produce high-performance MDF at
lower cost than wood-based MDF is basically linked to the possibility of improving the water repelling properties of the straw-based MDF. However, the chemical composition, fibre length and amount of dust generated are established and contribute to the poor water resistance.

![Figure 7.1-7](image)

**Figure 7.1-7** Thickness swelling of straw MDF vs. average density. Different types of straw (Chinese Chi, and Swedish Swe); type of UF resins (Urea-Formaldehyde UF, Melamine-modified UF resin, UMF-1, UMF-2, and Phenol modified, UFMP) and resin content are plotted. The straw MDF was produced by different pretreatment by addition of Acid (Ac), or water (Wa).

The thickness swelling of straw MDF was dramatically reduced by increased average density of the straw MDF panels. This improvement of MDF properties is also typical for wood-based MDF. **Figure 7.1-7** shows improved TS by increased resin content and by increased melamine content of the melamine-modified UF resins. The hydrophobic response of the straw MDF was improved as the melamine component in the UF resin or the resin level was increased. Furthermore, straw MDF loaded with the special resin mixture containing both melamine and...
phenol clearly demonstrated improved water repelling properties, see \((U M P F = 14\%, \text{ Chi., Ac.})\). The effect of acid pre-treatment of straw or the source of investigated wheat-straw materials was not clearly demonstrated. The water pre-treatment of size-reduced straw \((U M F-2 = 17\%, \text{ Chi., Wa.})\) indicated lower TS than acid pre-treatment of size-reduced straw \((U M F-2 = 16\%, \text{ Chi., Ac.})\). However, the most probable explanation for the TS reduction is the extra resin content +1\% of the water treated straw. The variables expected for improvement of thickness swelling of straw MDF can be summarised as follows;

- Increased density of straw MDF panels
- Increased resin content
- Increased melamine (phenol) content in the resin

The outcome of this investigation of TS is in agreement with the processing of wood-based MDF. The work to get adequate MDF from straw is mainly dependent on the careful raw-material handling and pressurized defibration to get suitable fibre and low levels of small particles, straw fragments, and dust. The properties of straw MDF panels can be controlled by the selection of a proper melamine-modified UF resin. The melamine content in the UF resin or the resin content can be adjusted for required properties. Alternatively, the average density of the wheat-straw MDF can be increased for improvement of TS and mechanical properties.

### 7.2 Manufacture of rice-straw MDF

Rice-straw \((\textit{Oryzae sativa} \text{ L.})\) was investigated as raw material in combination with methylene diphenyl diisocyanate (MDI) adhesive to manufacture high-performance MDF/HDF. This investigation was performed in pilot-plant scale and in similar process such as the manufacture of wheat-straw MDF (see chapter 7.1). However, deviating process methods was the water soaking and the resination of MDI that was performed after the drying step in a resin drum-blender. The rice-straw MDF/HDF exhibited properties that matched the properties of ordinary wood-based MDF. Reported investigations of fibreboard production based on rice-straw are less frequent than of wheat-straw and the rice-straw materials is often combined with other raw materials (Hiziroglu et al., 2008) or used for production of thermoplastic composites (Habibi et al., 2008). Moreover, production of Hard Boards from rice-straw pulp has also been reported (Mobarak et al., 1975). The more popular wheat-straw processing and pressurized defibration differ slightly compared with the rice-straw processing.
7.2.1. Rice-straw preparation, defibration, and fibre quality

In this study the rice-straw preparation system is illustrated in Figure 7.2-1. After cleaning, size-reduction, and screening the rice-straw was soaked in water for 24 h before defibration. Addition of pH reducing chemicals was unnecessary for curing of the MDI resin.

![Diagram of rice-straw fibre preparation system in an MDF pilot plant](image)

The production of rice-straw fibre was investigated at two defibrator housing pressure conditions to compare the fibre quality in a pre-trial (PT) at 0.6 MPa and main trial (T) at 0.5 MPa. Samples of the refined rice-straw fibres were analyzed by the PQM™1000 system. The fibre properties from the pre-trial and the main trials are shown in Table 7.2-1.
Table 7.2-1
Rice-straw fibre samples from a pre-trial (PT) and main trial (T), measured in PQM™1000 fibre classifier and Pulmac Instruments, 0.15 mm slot. Only the pH of the main trial rice-straw fibre material was measured.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Units</th>
<th>PT (1)</th>
<th>PT (2)</th>
<th>T (1)</th>
<th>T (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of fibre</td>
<td>#</td>
<td>300091</td>
<td>295531</td>
<td>263900</td>
<td>217728</td>
</tr>
<tr>
<td>Average length</td>
<td>mm</td>
<td>0.87</td>
<td>0.84</td>
<td>0.86</td>
<td>0.99</td>
</tr>
<tr>
<td>Average width</td>
<td>μm</td>
<td>27.6</td>
<td>28.2</td>
<td>31.1</td>
<td>30.3</td>
</tr>
<tr>
<td>Curl index</td>
<td>%</td>
<td>11</td>
<td>11</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Coarseness</td>
<td>mg/m</td>
<td>0.28</td>
<td>0.29</td>
<td>0.31</td>
<td>0.36</td>
</tr>
<tr>
<td>Number of shives</td>
<td>no/g</td>
<td>21417</td>
<td>26229</td>
<td>28048</td>
<td>32575</td>
</tr>
<tr>
<td>Shive weight</td>
<td>%</td>
<td>13</td>
<td>17</td>
<td>19</td>
<td>24</td>
</tr>
<tr>
<td>Average shive length</td>
<td>mm</td>
<td>1.6</td>
<td>1.6</td>
<td>1.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Average shive width</td>
<td>μm</td>
<td>198</td>
<td>197</td>
<td>198</td>
<td>207</td>
</tr>
<tr>
<td>Shives &gt; 0.15 mm wide</td>
<td>%</td>
<td>14</td>
<td>18</td>
<td>21</td>
<td>30</td>
</tr>
<tr>
<td>Short fibres &lt; 1.45 mm</td>
<td>%</td>
<td>79</td>
<td>79</td>
<td>80</td>
<td>72</td>
</tr>
<tr>
<td>Dust &lt; 0.45 mm</td>
<td>%</td>
<td>32</td>
<td>34</td>
<td>32</td>
<td>27</td>
</tr>
<tr>
<td>Pulmac 0.15 mm</td>
<td>%</td>
<td>15</td>
<td>20</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>-</td>
<td>-</td>
<td>6.6</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Measurement of the produced rice-straw fibre samples revealed homogenous fibre length distributions. The average length of the rice-straw fibre was approximately 0.9 mm, and the average fibre width was in the range of 28 – 32 μm. Rice-straw fibres from the main trial were a little longer than those from the pre-trial. The shive weight was also higher and in the range of 20 – 24%, compared to a shive weight of 13 – 17% from the pre-trial. The amount of shives is not critical for fibreboard properties in the same way that refining of fibres is critical for paper in mechanical pulping (Labosky et al., 1993). The shive weight of wood-based fibreboards can be in the range of 20 – 30%. The amounts of short fibre, straw fragments and dust in this investigation were defined as the amount of fibres shorter than 1.45 mm and the dust part shorter than 0.45 mm, respectively. Table 7.2-1 lists the contents of short fibres and dust content for the pre-trials PT(1) and PT(2) and the main trials T(1) and T(2). The pre-trials displayed higher dust contents 32 – 34% than the main trials 27 – 32%. Increased input of thermomechanical energy on the rice-straw causes a reduced fibre length and shive content.
Defibration of straw is perhaps not so common and more complex than refining of wood-based materials. The fibre quality, amount of dust, amount of shives, and fibre length must be firmly balanced to achieve the best fibreboard properties. The pH of the rice-straw fibre was approximately 6.5. The produced rice-straw fibre was of an acceptable fibre quality for straw MDF manufacture.

### 7.2.2. Mechanical properties of rice-straw fibreboards

The fibreboards were produced at three different resin levels: 3%, 4%, and 5%. Moreover, two different methods were tested to avoid adhesion (sticking) of fibreboards to the press plates: usage of paper sheets during pressing or addition of a press-release agent sprayed on intermediate steel plates. The benefit of using a press-release agent is of outermost importance for an effective full-scale production in continuous pressing of wood-based MDF.

![Diagram showing Internal Bond (IB) of rice-straw MDF/HDF at different MDI-contents and average fibreboard density](image)

**Figure 7.2-2** Average IB of rice-straw MDF/HDF at different MDI-contents and average fibreboard density. MDI=3%, MDI=4%, and MDI=5% represent different resin contents in MDF and paper sheets applied in hot-press as protecting layers. MDI=3% (PR) and MDI=5% (PR) represent resin content in MDF and spraying of press-release (PR) agent on steel plates before pressing.

**Figure 7.2-2** shows IB of rice-straw MDF/HDF for different MDI resin contents, different average densities, and different methods of press release. The influence of the average density and resin content on IB is significant. Increased density and resin content improve the MDF/HDF strength properties. High average densities of MDF panels for trials at (MDI=5%, 1060 kg/m³) were achieved, and consequently, a
high IB was observed (2.6 MPa). The average density and the MDI resin content are perhaps the most pronounced variables affecting the strength properties of fibreboards for traditional wood-based raw materials, for normal defibration conditions, and fully cured thermosetting adhesive (Suzuki and Kato, 1989; Wong et al., 2000; Han et al., 2001b; Halvarsson et al., 2009).

The rice-straw fibreboards produced using paper sheets or press-release agent exhibited roughly the same IB properties when compensating for density, and more importantly, all produced rice-straw fibreboards displayed excellent IB strengths. The requirement in ANSI A208.2-2002 standard for interior applications is defined to IB > 0.5 for grade 120 and IB > 0.6 MPa for grade 130. Furthermore, the average MDF density is typically between 500 – 1000 kg/m$^3$.

![Diagram](image_url)

Figure 7.2-3  Modulus of rupture (MOR) vs. fibreboard density at different MDI-contents. MDI=3%, MDI=4%, and MDI=5% represent different resin contents in MDF and paper sheets applied in hot-press as protecting layers. MDI=3% (PR) and MDI=5% (PR) represent resin content in MDF and spraying of press-release (PR) agent on steel plates before pressing. The ANSI, grade 120 and grade 130 requirements are represented by lines.

The bending properties of the rice-straw MDF/HDF included acceptable bending strengths. Figure 7.2-3 presents the modulus of rupture (MOR) as a function of average density. The numerical values of MOR of the rice-straw MDF/HDF were generally above the requirements in the MDF standard (ANSI, grades 120 and 130).
The different press-release methods had minor effects on MOR. The bending properties of conventional wood-based particleboards and fibreboards are strongly dependent on the average density (Shi et al., 2005). The rice-straw fibreboards also followed this density dependence. Additionally, a small improvement of the bending properties was observed for increased MDI resin content.

7.2.3. Thickness swelling of rice-straw MDF

The combination of lower amounts of lignin and more hemicellulose components contributes to inherently higher water swelling of most annual plant fibres compared to what is found for wood fibres (Sun et al., 1997; Rowell et al., 2000; Donaldson et al., 2001; Reddy and Yang, 2005). Unexpected low thickness swelling and water absorption factors were observed for produced MDF panels based on MDI resin and rice-straw fibres, as shown in Figure 7.2-4. Almost all tested fibreboards displayed swelling in the range of 15 – 30%.

Figure 7.2-4  Thickness swelling vs. fibreboard density at different MDI-contents. MDI=3%, MDI=4%, and MDI=5% represent different resin contents in MDF and paper sheets applied in hot-press as protecting layers. MDI=3% (PR) and MDI=5% (PR) represent resin content in MDF and spraying of press-release (PR) agent on steel plates before pressing. The ANSI, grade 120 and grade 130 requirements are represented by a line.
Increased MDI resin loading (MDI = 5%) show a TS-range of 15 – 25%. The requirements in the wood-based MDF-standard (ANSI, Grades 120 and 130) for approved MDF panels are defined as a thickness swelling of 1.5 mm, or lower than 50%, for sanded MDF thicknesses of approximately 3.0 mm. Furthermore, the different press-release methods had no effect on the water swelling. For higher densities, the water repelling properties seemed to be improved. Increased loadings of MDI resin also reduced the thickness swelling. The MDI adhesive is formaldehyde-free and is suitable for fibreboard products where the demand for minimal formaldehyde emission is required.

7.3 Manufacture of binderless straw MDF

The manufacture of the non-resin wheat-straw MDF was performed in pilot-plant scale similar to the wheat-straw MDF process (see chapter 7.1). No resin was added but instead the chemical component (Fenton’s reagent) was introduced into the defibration process. The fibreboard properties of the non-resin wheat-straw MDF were of poorer quality than the ordinary straw MDF. The expected high thickness swelling of the straw fibreboards was compensated for by the addition of a small amount of wax and CaCl₂ as a water repelling agent. Paraffin wax or wax emulsions are added in small quantities 0.5 – 1.0%, to improve the water resistance of the MDF. Fibreboards made using annual plant materials and agricultural waste have even worse water-resistant properties than wood (Sauter, 1996; Markessini et al., 1997; Han et al., 2001b; Mantanis and Berns, 2001; Wasyliciw, 2001; Ye et al., 2007). Another way to improve the hydrophobic properties of the fibre is to add small quantities of salts containing di- or trivalent cations (Westin et al., 2001). The most frequently used salt in the papermaking industry is aluminium sulphate. Below pH 9, the cations are primarily adsorbed to the pulp fibres by electrostatic interactions with carboxylic groups in the lignocellulosic material. The electrostatic interactions result in adsorption of small species or colloids on the fibre surface, altering the surface properties of the fibres (Ohman and Wagberg, 1997; Kato et al., 2000). Improved swelling resistance in wood-based fibreboards has been reported after addition of CaCl₂ (Westin et al., 2001; Widsten, 2002)

7.3.1 Production of non-resin wheat-straw fibre and properties

The pilot-plant manufacture of the non-resin fibreboard based on wheat-straw are much the same as the Mid Sweden University & Metso method of manufacturing straw MDF and HDF (see chapter 7.1). Chemicals such as hydrogen peroxide, co-reactants and calcium chloride (CaCl₂) were added to the Defibrator™ system instead of using a binder such as MUF resin. The defibration, forming and pressing of the activated fibres were divided into four major trials denoted RA, RB, and, RC displayed in Table 7.3-1.
Table 7.3-1

Amount of added chemicals, wax, and melamine-modified urea-formaldehyde MUF resin for the different straw fibreboard trials (RA–RE) based on dry wheat-straw

<table>
<thead>
<tr>
<th>Trial</th>
<th>Hydrogen peroxide (%)</th>
<th>Ferrous sulphate (%)</th>
<th>Calcium chloride (%)</th>
<th>Wax addition (%)</th>
<th>MUF Resin addition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA</td>
<td>2.5</td>
<td>1</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RB</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RC</td>
<td>4</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RD</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RE</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Trial RD was only used to produce fibres for evaluation of the fibre properties and was produced without the addition of chemicals during refining. The reference wheat-straw MDF in trial RE had been produced in an earlier investigation (see chapter 7.1). The pH of the wetted straw reference sample was 7.8. In this investigation the size-reduced straw was pre-treated with sulphuric acid to reduce the pH of straw and to act as a catalytic component for activation of the straw lignocellulosic, see Table 7.3-2.

Table 7.3-2

The pH and pH-buffering capacity of straw and straw fibres samples after different chemical treatments and the addition of chemicals based on dry wheat-straw

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Straw</th>
<th>Straw</th>
<th>RA</th>
<th>RB</th>
<th>RC</th>
<th>RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straw pre-treatment</td>
<td></td>
<td>Water</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Acid</td>
<td>Water</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.8</td>
<td>4.7</td>
<td>3.3</td>
<td>3.1</td>
<td>3.1</td>
<td>5.7</td>
</tr>
<tr>
<td>pH-buffering</td>
<td>mL</td>
<td>14.5</td>
<td>8.2</td>
<td>2.8</td>
<td>1.8</td>
<td>2.0</td>
<td>8.5</td>
</tr>
<tr>
<td>Addition of Chemical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2SO4</td>
<td>%</td>
<td>-</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>-</td>
</tr>
<tr>
<td>H2O2</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>4</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>CaCl2</td>
<td>%</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The lowest pH value (pH = 3.2) and the least amount of titration solution (1.8 mL) were observed after acid pre-treatment of the straw in combination with the addition of 4.0% hydrogen peroxide to the defibrated fibres (trials RB and RC).
Samples of defibrated wheat-straw fibres were analyzed in the PQM 1000 fibre classifier system. The fibre properties from all the separate trials (RA to RD) are presented in Table 7.3-3. Varying the amounts of hydrogen peroxide and calcium chloride had no major effect on fibre length, width or curl. Defibration of straw materials will always result in high levels of dust and oversized fibre bundles compared to wood-based materials.

Table 7.3-3
Properties of samples of straw fibre from trials RA to RD, measured in PQM™1000 fibre classifier and Pulmac Instruments, 0.15 mm slot. Average values calculated for two separate fibre samples

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>RA</th>
<th>RB</th>
<th>RC</th>
<th>RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average length</td>
<td>mm</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
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</tr>
<tr>
<td>Average width</td>
<td>μm</td>
<td>25</td>
<td>26</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>Curl index</td>
<td>%</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Coarseness</td>
<td>mg/m</td>
<td>0.34</td>
<td>0.36</td>
<td>0.40</td>
<td>0.35</td>
</tr>
<tr>
<td>Shive weight</td>
<td>%</td>
<td>15</td>
<td>18</td>
<td>17</td>
<td>19</td>
</tr>
<tr>
<td>Short fibres &lt; 1.45 mm</td>
<td>%</td>
<td>68</td>
<td>68</td>
<td>69</td>
<td>65</td>
</tr>
<tr>
<td>Dust &lt; 0.45 mm</td>
<td>%</td>
<td>21</td>
<td>21</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>Pulmac 0.15 mm</td>
<td>%</td>
<td>17</td>
<td>19</td>
<td>20</td>
<td>24</td>
</tr>
</tbody>
</table>

7.3.2. Non-resin straw MDF properties

The fibreboards manufactured seemed to be of sufficiently high quality after pressing. The best results were found for high loading of hydrogen peroxide (4%) and densities above 1000 kg/m³. The high-density range of produced straw fibreboards was above the typical density range of MDF and should be considered high-density fibreboard (HDF). Hydrogen peroxide–activated fibreboards showed moderate mechanical properties compared to the reference straw fibreboards, glued with melamine-modified UF resin. The internal bond and bending properties, modulus of rupture were acceptable (Figure 7.3-1 and 7.3-2). The water resistance or thickness swelling was the main dilemma. Even though the addition of calcium chloride improved the fibreboards properties, the water-swelling properties were adversely affected. None of the manufactured straw fibreboards met the European wood-based standard for MDF (EN 622-5, 2006).
Figure 7.3-1 shows the IB of the non-resin straw fibreboards as a function of the average density. The IB was below or close to the requirements in the standard for MDF. The enhanced adhesive effect obtained by activation of the wheat-straw fibres by hydrogen peroxide is obvious. However, the reference straw MDF glued with a commercial MUF-resin showed satisfactory strength levels.

The most probable contribution of the mechanical strength of the straw MDF is the formation of covalent bonds between chemical groups on adjacent fibres surfaces. High water absorption of the finished fibreboards is observed and could be regarded as contradictory to the suggested covalent bonding. However, it should be remembered that hydrogen peroxide oxidises the fibre material and increases the overall number of charged groups, and thus, the prerequisites for water sorption. Other adhesive effects such as electrostatic interactions between adjacent fibres might also be possible when divalent metal ion salts are added. Increasing the H₂O₂ from a level of 2.5 to 4.0% improved the strength of the fibreboards. The internal bond was increased from approximately 0.45 MPa to around 0.65 MPa at a density of 1000 kg/m³ or higher. Finally, the addition of CaCl₂ seemed to increase the IB strength (compare trials RB and RC).
Figure 7.3-2  Modulus of Rupture (MOR) of wheat-straw fibreboards as a function of average density. The line represents requirements in the MDF standard EN-622-5: 2006. See Table 7.3-2 for further explanation of the figure legends.

Figure 7.3-2 shows the MOR as a function of the average density. The different hydrogen peroxide loadings and calcium chloride additions had only minor effects on the MOR. Almost all fibreboards above densities of 975 kg/m$^3$ met the requirements in the MDF standard. The reference straw MDF panels showed numerical MOR values above 40 MPa. Thickness swelling of the non-resin wheat-straw MDF showed extensive water swelling levels (Figure 7.3-3). The lower amount of added hydrogen peroxide (2.5%, trial RA) during the defibration process generated straw MDF of TS as high as 190% at densities less than 900 kg/m$^3$. Increased hydrogen peroxide addition (4%, trial RC) reduced the TS to a range of 110 – 130% at densities in the level of 950–1000 kg/m$^3$. Furthermore, the loading of 2% calcium chloride and 4% hydrogen peroxide (trial RB) improved the TS of produced straw MDF further to approximately 85 – 95% thickness swelling in the density range of 950 – 1000 kg/m$^3$. 
Figure 7.3-3  Thickness swelling of wheat-straw fibreboards as a function of average density. The line represents requirements in the MDF standard, EN-622-5: 2006. See Table 7.3-1 for further explanation of the figure legends.

The increased oxidation of the straw lignocellulosic improved the bonding between adjacent fibres, contributing to increased strength and reduced TS of the straw MDF. High loadings of hydrogen peroxide (4%) and the addition of calcium chloride (2%) reduced the thickness swelling by approximately 30%, from TS of 130% (trial RC) to a level of 90% (trial RB). The lowest thickness swelling was achieved for the reference straw MDF, approximately 20%, and which was composed of wheat-straw, UMF resin, and wax (trial RE).

7.4. Thickness swelling and water retention value

Wood, straw, and other lignocellulosic materials change dimensions with varying moisture content due to the hydrophilic functional groups attached to the cell wall polymers, such as hydroxyl, carboxyl, phenolic and oxygen containing groups that attracts water molecules. Adsorption of water may swell the cell wall, and the lignocellulosic fibre swells to a saturated level. The functional groups on the lignocellulosic polymers give rise to a concentration gradient of ions between the interior of the fibre wall and the external solution. Due to the osmotic pressure, an expansion of the cell wall appears. The expansion is stopped by the structural integrity created by the lignocellulosic structural components within the fibre (Wagberg, 2007).
MDF is a hygroscopic product that changes in dimension as the moisture content changes. The water resistance and dimension stability of MDF are complicated to understand and control. In a review of thickness swelling of Hardboard it was concluded that several material and processing variables influence the thickness swelling behaviour (Caril, 1997). These variables were categorized as:

- Processes that chemically modify fibres by heat or addition of chemical additive.
- The specific type of the raw material, HW, SW or mixtures.
- Preventing build-up of residual compressive stresses within panel during hot pressing or relief of these stresses after pressing.
- Use of adequate adhesive.
- Use of bulking or sizing additives.

This is also true for the dry-process fibreboard and increased content of adhesive has been shown to improve the TS of wood-based composites.

Compared to thin hardboards, MDF itself has a variation of the density in the thickness direction, a vertical density profile (VDP). The VDP is characterised of high surface density layers and in between a core layer of lower density. The MDF will swell dissimilar during a water soaking test and expand differently, depending on the actual densities and thicknesses of the surface and core layers. Regarding the fibrous straw material, the lignocellulosic components consist of different amounts and proportions of various chemical structures compared to wood. The hemicellulose content in wheat-straw is higher and the lignin content is lower than wood-based material (Schmidt et al., 2002). Additionally, silicon is present in much higher levels in straw than in wood-based furnish. All these chemical components have an influence of the water absorption and the thickness swelling of MDF. Finally, the fibres are bonded together by an adhesive that has specific water resistance properties due to the designed composition and chemical structure of the melamine-modified UF resin. The thickness swelling of MDF will be dependant on the melamine content in the resin. The PF and MDI types of adhesives shows perhaps the most promising swelling properties and can be used for exterior applications of MDF (Pizzi, 1994).

Methods for analysis of dimensional stability and water resistance of wood-based MDF are many. The most common methods are the thickness swelling (variation perpendicular to the plane) and water absorption (EN 317, 1993; American Society for Testing Materials, 2006). Another related property is the length expansion (variation in the MDF plane) but not analysed inhere. The critical water resistance properties are regulated in standard for MDF (EN 622-5, 2006) and different maximum thickness swelling is allowed for different MDF thicknesses.
thicknesses less than 6 mm has general a high average density and is allowed to swell up to 30%. MDF of thicknesses above 18 mm is often of lower average density and only allowed to swell 6%. The resin level, resin characteristics, density profile, and average density of the MDF are however not specified in the requirements in standards for MDF. Consequently, better methods and understanding of various processes and material parameters are needed to improve the water repelling properties of MDF.

7.4.1. Water retention value (WRV)
The swelling of cellulose, TMP, and CTMP fibres can be investigated by the measurement of the remaining amount of water in fibres after centrifugation at high rotation speed, or the water retention value (WRV), (Hopner et al., 1955). WRV is often used for measurements of the swelling behaviour of fibres for pulp & paper applications. Fibre swelling promotes bonding between cellulose fibres and consequently improves the strength in paper. However, MDF fibres are typically defibrated, blowline resinated, and dried before hot-pressing. Contrary to chemical pulp, an adhesive (oligomer, polymer) is added to the produced fibre. Only insignificant amounts of lignin, hemicellulose are removed from the cell wall during processing. The formation of an open porous fibre wall structure is not the case in the MDF process. Still the MDF fibre is expected to show a broad range of water swelling behaviour due to the defibration and drying process conditions, in combination with the amount and nature of the adhesive applied.

The swelling of mechanical pulp is restricted by the fibre structure. It has been shown that refining does not significantly change WRV of the long-fibre fraction of a mechanical pulp (Law et al., 1998). The water retention value is sometimes used to measure the swelling of alkaline chemical-mechanical pulps (Zanuttini and Marzocchi, 2003). The lignin swells much less than the carbohydrates (Lindstrom and Westman, 1980) and removal of lignin thus leads to increased fibre swelling (Stone and Scallan, 1967; Stone et al., 1968). Moreover, an increase in the temperature result in a rapid swelling of lignin containing pulps at temperatures approximately above 60 °C, which is due to the softening of lignin (Eriksson et al., 1991). The water swelling of the fibre wall is affected by many factors for example mechanical or chemical treatment. Defibration and production of fibres for MDF always involve a drying step. The dry content of typical MDF fibre is in the range of 8 – 12%. When chemical pulp fibres are dried, the internal pore volume shrinks if fibres are re-suspended into water and the original water-swollen state is not regained. The explanation of this behaviour is described as formation of hydrogen bonds and thermal cross-linking of cyclic esters, lactones. (Diniz et al., 2004). Nevertheless, the process of drying fibres (hornification) causes a significant loss of large pores (Stone et al., 1968). On the molecular level the adsorbed melamine-
modified urea-formaldehyde resin consists of soluble oligomers that will partially condense into an insoluble cross-linked resin network (Pizzi, 1983). A gel-like conformation based on the MUF resin is created and located on the fibre surfaces. Similar behaviour is well-known for cellulose fibres in pulping but here the increased WRV is described as gel formation of the outermost cellulose fibre surface and demonstrated as improved strength of the finished paper. Moreover, the MUF resin penetrates into holes, cavities, and large pores of the fibre. Available water is adsorbed and incorporated into the lignocellulosic polymers in the cell wall and the partly cross-linked urea-formaldehyde oligomers. The increased WRV of resinated fibre is probably a combination of the formed urea-formaldehyde gel content and the improved accessibility of water and consequently fibre swelling.

![Graph showing WRV of wheat-straw MDF fibre measured after approximately 30, 60 and 180 minutes soaking. MUF resinated wheat-straw fibre 13% dry basis (- -). Un-resinated wheat-straw fibre (- -).](image)

Figure 7.4-1  WRV of wheat-straw MDF fibre measured after approximately 30, 60 and 180 minutes soaking. MUF resinated wheat-straw fibre 13% dry basis (--). Un-resinated wheat-straw fibre (-- -).

Dynamic swelling or WRV of resinated and un-resinated straw MDF fibre was investigated. The production of wheat-straw fibres were processed and dried at similar process conditions. The resinated fibre samples contained a conventional MUF resin at a resin content of 13%. It is general accepted that when added, resin partially covers the fibre surface and a part of the resin will penetrate into the cell wall (see chapter 4.1). The fibre samples were prepared in water by soaking fibres for 30 to 180 minutes at a mild stirring of the straw fibre suspensions before the WRV analyses. **Figure 7.4-1** shows the WRV as function of soaking time of wheat-straw fibres. The WRV of both MUF resinated and unresinated fibres increased...
with soaking time and the un-resinated fibres increased at a higher rate than the MUF resinated straw fibres. Furthermore, the MUF resinated straw fibre samples showed a lower WRV level than the un-resinated fibres. During processing the MUF resin was injected into a flow of steam and fibre at a high speed and high turbulence level in the blowline. Small droplets are distributed on the fibre surface and the ideal situation is to form a sock of adhesive around the fibre. After drying the applied MUF resin was deposited on the fibre and migration of the MUF resin is unlikely. The added hydrophobic type of melamine-modified UF resin will change the surface characteristics of the fibre and reduce the fibre swelling compared with the unresinated fibre samples. As a result the addition of MUF resin reduces the WRV compared with the unresinated fibre.

![Graph showing Thickness swelling (TS) of MDF (■) and the Water retention value (WRV) of resinated fibre (○) as a function of resin content.](image)

Figure 7.4-2  Thickness swelling (TS) of MDF (■) and the water retention value (WRV) of resinated fibre (○) as a function of resin content.

The ability of resinated fibres to adsorb water is most likely dependant on the fibre cell wall characteristics. The suggested hypothesis is that the type and the amount of resin added to the fibre have an influence on swelling of fibre and of the WRV, which would be possible to connect to the thickness swelling of the finished MDF. This study was an attempt to evaluate the possibility for prediction of the thickness swelling of MDF based on measurements of the fibre swelling property.

The influence of the MUF resin content on the thickness swelling of wheat-straw MDF, combined with the swelling of corresponding wheat-straw fibres, measured as WRV were investigated. The relationship between TS, WRV, and the resin
content were of interest. WRV is an indicator of liquid water accessibility and was measured after 2 hours soaking in gently stirred fibre suspension. Figure 7.4-2 shows TS and WRV as a function of added MUF resin at different resin content. The correlations between TS of the straw MDF, the WRV of corresponding dried resinated wheat-straw fibre as a function of the resin content (added MUF resin) was substantial.

- WRV(%) = 3.4x + 66 ($R^2 = 0.69$)
- TS(%) = 194e^{-0.35x} ($R^2 = 0.75$)

Increased resin content reduces the TS and corresponds to the acceptable theory concerning wood-based MDF. From the common knowledge of fibre swelling behaviour attributed to the lignocellulosic fibres the WRV relationship is contradictory. Resinated fibres are partly covered with resin and the fibre surface will contain less available lignocellulosic water-retaining chemical components as the resin content increases. The hypothesis presented inhere is related to the penetration of resin into the fibre cell wall according to Cyr (Cyr et al., 2008). And the possibility to block cracks, cavities, and large pores in the cell wall and consequently reduce the amount of accessible water. Zhang reported that WRV in untreated lyocell fabrics is not changed by the treatment with any additive polymers of binders and hardeners (catalysts). The polymer addition was perhaps of lower concentration and the lyocell treated fibres displayed low WRV of approximately 35% (Zhang et al., 2006).

However, an alternative explanation of the WRV increase of resinated MDF fibres can be presented. Water adsorbed on the resinated fibres during soaking has a more complex mechanism for desorption and transportation during centrifugation. Water can be trapped in the resinated fibres and result in increased WRV as the resin content increase. Resinated fibres can be described as a small tube covered with a thin sock of resin. In the soaking process water has a relatively long time for diffusion and penetration into the resin covered tube (resinated fibre). The following WRV analysis and ultra-centrifugation is a fast process and water can be trapped in the resinated fibres. Moreover, increased resin content implies a thicker layer of the resin and consequently an amplified resistance of water for desorption.

### 7.4.2. Thickness swelling mechanism of MDF

During the initial step of hot-pressing the compression deforms the dry and resinated fibres in the fibre mat to a rather flat geometry. The adhesive cure in the hot surface layers and the flat fibre geometry is consolidated. The press-platens are slightly opened and the fibres in the core layer can regain to a more circular shape.
The subsequent compression (pressing) will increase the temperature in the core and finally cure the adhesive. Two high-density regions (surface layers) and a core of lower density is formed. The structural variations of the MDF have an influence on the properties. TS of the straw MDF was followed during 24 h soaking in water. Two main water swelling processes of fibre in the MDF panels were recognized, the conventional water adsorption (swelling) behaviour of the fibres, and the inherent recovery of the original fibre configuration called “spring-back”. These two mechanisms will contribute to the thickness swelling of the MDF. The later process is the irreversible swelling. Reports on the thickness swelling of separated thin layers of sliced MDF have been presented. The high density regions in the vertical density profile displayed higher TS and WABS than the lower densities in the core (Xu and Winistrofer, 1995; Xu and Winistorfer, 1996).

![Graph showing vertical density profile](image)

**Figure 7.4-3** Wheat straw MDF vertical density profile (VDP) at various times soaked in water during 24 h. Thickness swelling was measured after 1, 2, 4, 6, and 24 h.

In **Figure 7.4-3** the thickness swelling of a wheat-straw MDF specimen was investigated by measurements of the vertical density profile as a function of time. VDP-analyses were performed after 1, 2, 4, 6, and 24 h during soaking in water. The density profile of the straw MDF reference is represented by a thick black line. Moreover, a distinct jump of the core density could be observed after 24 h soaking, but this is due to a defect of the fibre material in the MDF.

Initially, the core density was approximately 760 kg/m³ and the surface densities were roughly 1250 kg/m³. The proposed thickness swelling mechanism can be divided into swelling of the core and surface layers (**Figure 7.4-4**). The swelling of
the core is rather conventional and starts when the water begins to penetrate into
the MDF specimen and the core density increases from a density of 760 kg/m$^3$ to
approximately 975 kg/m$^3$ after 24 h water soaking. The absorbed water increases
the mass and the weight of the MDF specimen, mainly in the beginning of the
soaking process.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Thickness swelling and density (surface and core) increase of wheat straw
MDF as a function of water soaking time. Measurements after 1, 2, 4, 6, and
24 h (TS is represented by a correlated dotted line).}
\end{figure}

The proposed mechanism of the surface layers swelling is more complicated.
When the high density surface layers absorb water, the surface densities are
notable reduced and a minimum surface density level is reached after one hour
(1150 kg/m$^3$). After a while, the surface densities continue to increase in the same
way as the core density. The initially penetrated water and moisture will probably
be adsorbed in the cell wall and not in the fibre lumen. It can be assumed that a
compressed fibre of flat geometry adsorbs water and start to regain a more circular
cross-section and increase volume. The adsorbed water softens the fibre cell wall
and together with osmosis (MDF spring-back) the total fibre volume increases at a
higher rate than the contribution from the water adsorption rate of the cell wall.
These two fibre swelling mechanisms result in a reduced surface density in the
beginning of the water soaking test (Figure 7.4-4). More water continues to
penetrate into the fibre lumen and the density increase due to the amount of
adsorbed water.

66
The density profile of the MDF soaked in water for 6 and 24 h shows a drop in the VDP-curve at approximately 10 mm and 11 mm thickness, respectively. The most probably explanation is small defects in the homogeneous fibre material such as a shive or poor resinated straw fragments. Different chemical and physical interfacial interactions of resin, fibres and shives contribute to dissimilar swelling in the fibre material. Reduced strength in the z-direction of the MDF specimen introduces cracks and bond failures. Consequently, the water can continue to penetrate into the MDF specimen and support the dissimilar thickness swelling, locally in the MDF until a sudden crack or delamination occurs. The delamination open the structure further and water can easily penetrate into the MDF and amplify the thickness swelling. The variation of TS of several tested MDF specimens can be difficult to interpret depending on the frequency of local shives and other fragments containing poor resinated surfaces.

7.4.3. Summary

The improvement of water resistance of straw MDF is a major challenge to develop a sound economical and high performance quality of straw MDF. The resinated fibre contributes in the end to a more water resistance straw MDF. The relationship between thickness swelling of straw MDF and the water retention value of straw fibres in combination with the amount of adhesive was correlated. Improved thickness swelling of the finished MDF and increased swelling of resinated fibres, measured as WRV, was achieved as a function of the resin content.

Thickness swelling of MDF is assumed to be composed of two structural segments, the surface layers and the core. Depending on density, layer thickness, fibre characteristics, fibre quality, fibre swelling behaviour, and the amount of adhesive and type, the prediction of the final thickness swelling differ from the conventional models of mechanical properties as IB, MOR, and MOE. A more specific description of the fibre swelling properties of resinated fibres must be investigated and developed. The understanding of the complex interaction between adhesive (MUF resin), lignocellulosic, water, and the MDF fibre structure is only in an initial state and more investigations must be preformed to elucidate the swelling mechanism of resinated fibres and MDF. An interesting opportunity exists in measurements of the fibre swelling to predict the water resistance of finished MDF and improve the quality of straw MDF and wood-based MDF.
8. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The manufacture of straw MDF was based on different straw species and adhesives. Wheat-straw and melamine-modified urea-formaldehyde (MUF) resin was blowline blended. Rice-straw and methylene diisocyanate was blended after the fibre drying process in a resin drum-blender. Wheat-straw fibre was activated in the blowline by the addition of Fenton’s reagent (ferrous chloride and hydrogen peroxide) for production of non-resin MDF panels. The MUF/wheat straw MDF panels were approved according to the requirements of the EN standard for MDF for interior applications (EN 622-5, 2006). The non-resin wheat-straw panels showed moderate MDF panel properties and were not approved according to the EN-standard. The MDI/rice-straw MDF panels were approved according to requirements of the standard for MDF of the American National Standard Institute (ANSI A208.2-2002).

Size-reduced wheat straw was screened and separated in different fractions. The different straw fractions indicated high levels of ash and inorganic components. The pH, pH-buffering capacity, ash, and silicon contents in the ash increased as the wheat straw particle sizes were reduced. The straw fraction less than 0.2 mm, contained a high ash content 15% and silicon content in the ash 18%. Effective size-reduction of straw and removal of small size particles, fragments, and dust was beneficial for the MDF panels. Moreover, the pH of the straw can be reduced in a pre-treatment process by addition of acid before defibration for improved curing of urea-formaldehyde resins.

Pressurized defibration of the straw was performed in pilot-plant scale. The best fibre quality of the wheat-straw was achieved at pressures of 0.6 – 0.7 MPa and retention times of 2 – 3 min. The rice-straw was defibrated at a pressure of approximately 0.6 MPa and a retention time of 1 min. The fibre quality was measured by the PQM 1000 system and the fibre lengths of wheat and rice-straw were in the range of 0.9 – 1.0 mm. The amount of dust and straw fragments less than 0.45 mm was below 30%.

The mechanical strength and physical properties of the straw MDF panels, IB, MOR, MOE, and TS were strongly depending on the average density and the resin content. The observed MDF properties were improved as a function of density and the resin content. Different pre-treatments and the origin of the wheat-straw displayed no major influence on the MDF properties. Increased melamine content of applied MUF adhesive strengthened the internal bond and improved the water resistance. The melamine content in the MUF resin did not affect the bending
properties. Rice-straw MDF was produced at resin contents of 3, 4, and 5%. The mechanical and physical behaviour of rice-straw MDF was similar compared with the wheat-straw MDF panels. Improved properties of MDF panels were observed as the density and resin content increased. Moreover, two different methods of press-release were investigated, adding intermediate paper sheets or spraying of press-release agent on steel press plates before pressing. No significant difference between the two press-release methods was observed of the MDF panel properties.

The manufacture of binderless (non-resin) MDF was based on wheat-straw. The wheat-straw was pre-treated with steam, hot water, and sulphuric acid before pressurized defibration. Adhesive bonding between fibres was initiated by activation of the fibre surfaces by an oxidative treatment during the defibration process. Fenton’s reagent (ferrous chloride and hydrogen peroxide) was added into the blowline. Two different levels of hydrogen peroxide were applied, 2.5% and 4.0%, respectively. Increased levels of hydrogen peroxide improved the mechanical and physical properties of the straw MDF panels. The MOR, MOE, and IB were lower than those of conventional manufactured wheat straw fibreboards but close to the requirements of standard for MDF. Addition of a fibreboard water-repelling agent, calcium chloride (CaCl₂), improved the water resistance and reduced the thickness swelling by approximately 25%. The mechanical and physical properties of the binderless straw fibreboards are unacceptable. However, the use of these fibreboards in applications designed for dry conditions (interior use) is possible to some extent and improvements of the MDF panel quality can be achieved by optimization of added chemicals and process conditions.

The perhaps most difficult straw MDF property to overcome is the extensive water-swelling ability or the thickness swelling of straw-based MDF compared to wood-based MDF. The chemical structure of hemicellulose and lignin in straw is different and has different proportion than in most wood species. A higher ratio of hemicellulose and less amount of lignin contribute to an increased thickness swelling. Additionally, very high levels of ash are observed in straw, consisting of silicon and inorganic components. The chemical characteristics of straw indicate a more pronounced swelling ability of straw MDF compared with wood furnish. Water resistance adhesives are necessary at slightly higher resin contents than for wood-based MDF.

Improvement of fibreboard properties and especially the water resistance of straw MDF panels is a challenge. The swelling behaviour is different compared to wood-based MDF. One step further in the development of an acceptable thickness swelling of MDF, without a major increase of cost, is to investigate the relationship
between WRV, TS, and the amount and type of added adhesives. Modification of adhesive to better adapt the physical and chemical properties of straw-based MDF is necessary for improved properties. Another possibility to improve the MDF process and MDF panels is to develop the straw logistic, the interaction between producer and straw suppliers (farmers). Rejects from the straw size-reduction processes should be returned as ash into the soil and energy generated in the MDF mills. Essential mineral components are regained to the ecosystem and improve the growth and quality of the straw plants.
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*The future was better before*
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