

## Fundamental understading of pelletization

EFP-2005 project (33031-037). Summary report

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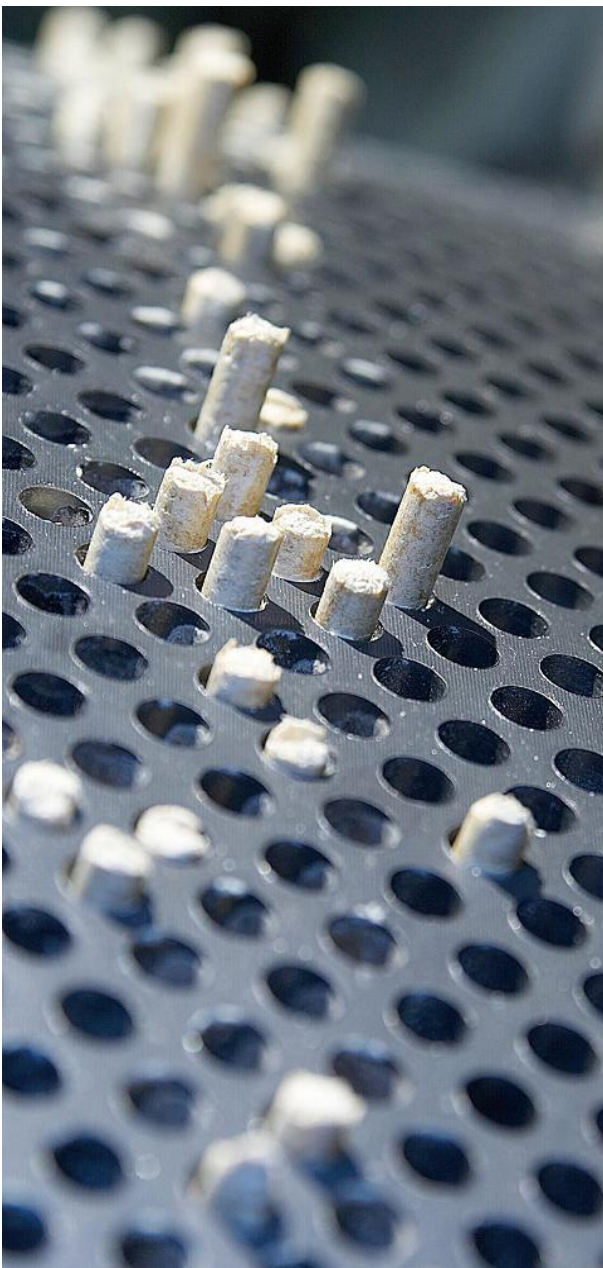
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June 2008

# Fundamental Understanding of Pelletization.

EFP-2005 project (33031-037)

Summary report



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**TEKNOLOGISK  
INSTITUT**



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## 1 Preface

The following report provides a summary of the work carried out during the EFP-project: Fundamental Understanding of Pelletization (33031-037 EFP-2005).

The work has been carried out in co-operation between the partners listed below:

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In addition to the present report the following papers, student reports and conference presentations have been published during the project:

- Jens K. Holm, Ulrik B. Henriksen, Kim Wand, Johan E. Hustad, Dorthe Posselt, Experimental verification of novel pellet model using a single pelleter unit, *Energy & Fuels*, **vol. 21**, 2446-2449, 2007.
- Jens K. Holm, Ulrik B. Henriksen, Johan E. Hustad, Lasse H. Sørensen, Toward an Understanding of Controlling Parameters in Softwood and Hardwood Pellets Production, *Energy & Fuels*, **vol. 20**, issue 6, 2686-2694, 2006
- Jens K. Holm, Ulrik B. Henriksen, Dorthe Posselt, Come giungere ad una comprensione basilare del processo di pellettizzazione, *Legno Energia*, **1**, 2006.
- Jens K. Holm, K. Wand, U.B. Henriksen, J. Hustad, L.H. Sørensen. Fundamentals of Biomass Pellet Production. *Proceedings of the 14th European Biomass Conference*, Paris, France, 2005.
- Jens K. Holm, Ulrik B. Henriksen, Johan E. Hustad, Lasse H. Sørensen, Fundamentals of biomass pellet production, MEK-ET-2005-01, Institut for Mekanik, Energi og Konstruktion, Danmarks Tekniske Universitet, 2005, ISBN: 87-7475-325-8.
- Jon V. Kringelum, Siv Sigvardsen, Jens K. Holm, Per Ottosen (2005), Large scale production and use of pellets - one year of operating experience, paper for the European pellets conference, 1-4 March, Wels, Austria.
- Bachelor thesis, Anders Bo Nielsen, MEK, DTU: Improvement of pelletization, 2007.
- Master thesis, Kim Wand, MEK, DTU: Mechanical Properties of Pelletization, 2005.

The conference presentations (references (1), (2), (3) and (4)) can be distributed upon request.

## 2 Acknowledgements

The work was financed by the Danish Energy Agency (33031-037 EFP-2005), DONG Energy and Vattenfall A/S. Valuable cooperation with the Biopellet factory in Køge is highly acknowledged.

### 3 Selected abstracts

*Energy & Fuels*, vol. 21, 2446-2449, 2007, ref. (5).

Pelletization of biomass for bioenergy purposes has established itself as an important step toward a reduction in the emissions of greenhouse gases. A novel pellet model describing the pressure forces in a press channel of a pellet mill has previously been published. The model gives a theoretical explanation of how the biomass-specific parameters, such as the friction coefficient and Poisson's ratio, influence the pelletizing pressure. The model showed that the pelletizing pressure increases exponentially as a function of the channel length. In the present paper, the pellet model is verified experimentally. When the back pressure needed to press pellets of different lengths out of the press channel is measured, it is shown that the pelletizing pressure does increase exponentially as a function of the pellet length. Second, the back pressures of the hardwood beech are higher than the corresponding pressures of the softwood pine for all tested pellet lengths. Least-squares fit of the model to the data shows that the fitted parameters are in agreement with values from the literature. The procedure for using a single pelleter unit as a means for simulating an industrial pelletizing process in a controllable way is described.

*Energy & Fuels*, vol. 20, issue 6, 2686-2694, 2006, ref. (6).

Production of biofuel pellets from hardwood, such as beech, is often very troublesome as observed in largescale pellet production plants, where reduction of capacity and frequent blocking may be experienced. The problems may be reduced through a laborious optimization procedure of the process conditions and the utilization of softwood and adhesive materials. To optimize and facilitate such a procedure, a deeper understanding of the fundamental physical-chemical mechanisms that control the pelletizing process is sought after by combining small-scale experiments and an advanced pellet production model. Mixtures of beech rich in corrosive alkali chloride salt, pine softwood, brewers spent grains (BSG), and inorganic additives are experimentally tested using a small-scale pellet mill. It was possible to pelletize a beech/pine mixture containing up to 40% (wt) beech. The addition of 15% (wt) BSG to the beech dust significantly facilitated the pelletizing process. The addition of necessary inorganic anti-slag and anti-corrosive compounds into pellets made of beech may enhance the problems in an unpredictable way. However, if the inorganic additives are added directly into BSG before mixing it with the beech dust, the material can easily be pelletized.

A pellet production model is developed that describes the pelletizing pressure variation along the press channels of the matrix. Equations based on differential control volumes are set up to describe the forces acting on the pellet in the matrix. Important model parameters are the sliding friction coefficient, the ratio of compression, and the material-specific parameters, such as the elastic modules and Poisson's ratio. Model calculations show how the variation in the model parameters significantly changes the necessary pelletizing pressure. Using typical material parameters of beech and pine, it is illustrated why beech, in accordance with the experimental test results, is more difficult to pelletize than pine.

*Proceedings of the 14th European Biomass Conference*, Paris, France, 2005, ref. (7).

Pelletizing experiments and theoretical modeling of the pelletizing process have been carried out with the aim of understanding the fundamental physical-chemical mechanisms that control the quality and durability of biomass pellets. A small-scale California pellet mill (25 kg/h) is used to test the pelletizing performance of two wood species, the hardwood beech and the softwood pine. In accordance with experiences from large-scale pellets production, the test

results show that the production of pellets from beech is significantly more troublesome than production of pellets from pine. Addition of 1 wt% calcium soap to the beech dust lowers the power consumption of the pellet mill. However, the calcium soap furthermore reduces the friction of the channels in the matrix, leading to lower durability of the produced pellets. It is proposed that the difference in pelletizing performance is a direct consequence of the difference in wood cell structure between hardwoods and softwoods, which in turn affects the mechanical properties of the biomass during pelletization. A novel model gives a theoretical basis for this finding.

#### *Light- and electron-microscopy, chapter 5.*

As demonstrated in this section, the structure of wood is complex and hierarchical, thus allowing for the specific mechanical properties giving wood its unique characteristics as a construction material. The presence of long tubular cells is important in modelling the behaviour of wood raw material in a channel press. A surprising degree of organized structure is preserved in the pressed pellets thus giving the pellet an overall density lower than the density of the cell wall material.

#### *Chemical characterisation of pellet materials, chapter 7.*

Neither Raman spectroscopy nor XPS showed any chemical differences in the bulk or surface of softspån material as a result of the pelletising process and therefore it is clearly not possible at this stage to suggest that chemical changes in this material could contribute to differences in the quality characteristics of fuel pellets. A more extensive investigation including, for example, longer Raman spectra collection times and more closely controlled incoming raw material quality for XPS in combination with other pellet materials, might provide a more definitive study than was possible in this investigation.

#### *Standards and standardization criteria, chapter 8.*

The research performed in this project is at a very early stage compared to the process of standardisation. The methods described in CEN with Technical Reports (TR), Technical Specifications (TS), Guidelines (pre-standards) and Standards are tested and discussed in projects and Working Groups over years in different institutions, universities and companies.

## **4 Fundamental understanding of pelletization.**

### **4.1 Introduction.**

One main objective of the European Union energy policy is increasing usage of bioenergy, mainly driven by a desire to lower CO<sub>2</sub> emissions and to reduce the dependency on fossil fuels. This aim of increasing use of bioenergy is expressed both on regional and national levels in different European countries. In Denmark, the debate concerning environmentally friendly energy and security of the energy supply has received increased attention at the highest political level.

One way to reduce CO<sub>2</sub> emissions is the utilization of biomass as an energy source. Overall, there is a large variety of biomass available. Typical sources are wood residues, agricultural residues and various industrial residues and waste products. An effective way to utilize biomass as a fuel is in the form of pellets.

Biopellets offer a safe, sound and convenient biofuel to bridge the energy gap in the transition away from fossil fuels. Biomass fuel pellets have several advantages compared to unprocessed biomass. The process of pelletization preserves the biomaterial thus ensuring the value as a fuel. Furthermore, the pelletized product is more or less standardised allowing trade within the internal market as well as on a global scale using overseas transports. The energy density is high (~18.000 kJ/kg) and handling and storing is less problematic and more cost effective due to the uniform size, high bulk density (~650 kg/m<sup>3</sup>) and low moisture content (~5 %). The uniform size makes the pellets suitable for small heating systems such as stoves and boilers for domestic use. However, the pellets are also used in full-scale power plants such as the highly efficient power plant Avedøre 2 in eastern Denmark, where up to 300.000 tons of wood pellets are used every year. By using pellets, it is possible to burn up to 100% pure biomass in existing coal-fired power plants. Furthermore, the electrical efficiency of pellet-fired plants can reach 45%, which is around 10% higher than the efficiency of conventional grate-fired plants.

Emissions of ultra fine particles from small pellet stoves are comparable to the emissions from existing oil-fired boilers. These numbers are a factor of 10-100 times smaller than the emissions of particles from conventional wood-burning stoves (8).

The production of pellets from biomass is cheap, safe and the industrial development is combined with low risks compared with other technologies to promote biofuels.

The market for biomass pellets is growing rapidly. A rough estimate is that the total world market amounts to around 7 million tons per year, but this number is increasing significantly day by day. The majority of pellets are made from sawdust and shavings obtained from sawmills and wood processing industries. To a lesser extent, agricultural waste products such as straw are used for the pellet production. However, the growing market for pellets increases the demand for raw materials and the need for alternative materials in order to secure the supply. The waste products from production of liquid biofuels (e.g. bioethanol) can also be converted to pellets and hence utilized as a fuel suitable for many different applications, thus increasing the energy efficiency of the production of liquid biofuels.

#### **4.1.1 Aim of project**

The pelletization of different types of biomass to fuel pellets is frequently met with production-related difficulties that until now have been solved on an ad hoc basis, resulting in no fundamental understanding of the pelletization process. The practical knowledge obtained is usually limited to the biomass in use and cannot necessarily be extended to other kinds of biomass. This hinders the flexible pellet production that is crucial for an effective use of biomass. The aim of the present project is to contribute to the development of such a fundamental understanding in a crucial way. It is the expectation that a significant amount of the biomass utilization for energy purposes in the future will be based on pellets, where a large part of the pellets will be produced in Denmark. In a longer term, it is the aim that the established knowledge should be used to improve and optimize the pellets production, lower energy uptake and broaden the range of biomass that can be pelletized. Finally, the results should reveal the basic relationships between the production process and the quality of the

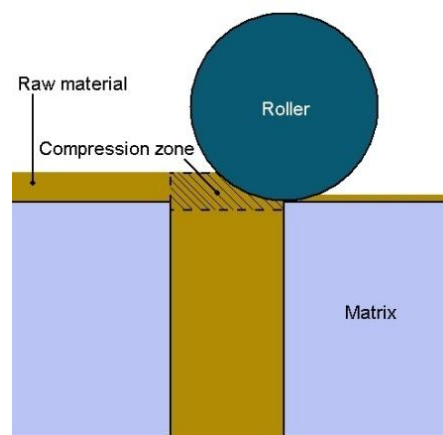


pellets. Furthermore, the established knowledge will contribute to the general research area of advanced structural biomaterials.

#### 4.1.2 State-of-the-art and motivation for the project.

Wood is one of the most widely used raw materials. The uses of wood include energy production, construction materials, paper production and production of chemicals. The properties of wood are controlled by complex interactions between the chemical and physical structure. The properties vary significantly between different wood species, in particular between hardwoods and softwoods. These differences are crucial for the industrial utilization of wood. Research within the area of wood science has contributed to the understanding of many of these differences. However, the initiation of biomass pellet production worldwide has raised several questions that cannot be answered by the existing knowledge in the field. In particular, there are fundamental differences that cause hardwoods to be much more difficult to pelletize than softwoods. During pelletization, many processes such as fibre softening, friction and auto adhesion are in play, but the nature and specific action of these processes in relation to different wood species are not understood. In addition, the basic question of how wood is “transformed” from powder to pellets during the passage through the channels of the pelletizing machine is also not understood in detail.

The majority of the pelletizing machines in use are of the ring matrix type. When the matrix is rotating, the adjacent roller forces the raw material into the channels of the matrix (Figure 1).



**Figure 1 Schematic drawing showing the zone of biomass compression in a ring matrix (6).**

To our knowledge, there are only two published reports on ring matrix pelletization (9) (10) and neither of these go into details concerning the fundamental mechanisms that control the compression forces during pelletization. Some modelling approaches have been put forward to understand the mechanical forces in play during pelletization. However, these models consider the compression against a fixed backstop as in a single pelleter unit (11) (12) (13) and not against a continuously moving backstop as for ring matrix pelletization. A brief review of the state of art for biomass densification has been published (13).

Hence, there is a substantial lack of knowledge related to the fundamental mechanisms that control the pelletizing process. As a direct consequence, the pellet production today is not

optimized; leading to high energy costs, low flexibility in relation to different materials and undesirable wear on the equipment. If the demands for an efficient use of biomass are to be achieved, these problems need to be addressed and solved.

In view of the arguments given above, a fundamental research EFP-project was initiated (14), with the aim of contributing to an improved understanding of pelletization processes. To achieve this goal, in-depth analyses of both the mechanical relationships and the biomass-specific structural changes taking place during pelletization are required. These investigations also involve adhesive chemistry. Studies of structural changes and binding mechanisms on the level of wood cells set a demand for advanced biophysical techniques. In order to be successful, these techniques presume a careful sample preparation and preceding characterization of the biomass.

The EFP-project concerns basic mechanical studies of pelletization carried out with a laboratory pellet mill and a single pelletizing unit. Equipment has been developed to measure pressure forces and temperature in order to study the influence these factors have on pelletization. A theoretical model describing the forces during the pelletization has been developed (6) (15). The model proposes an explanation for the difference in the pelletizing behaviour between hardwoods and softwoods. The experimental results from the pelletizing tests are in accordance with the model. In addition, a procedure for using a single pelleter unit to predict the performance of the ring matrix pellet mill has been developed (5).

The EFP-project is highly inter-disciplinary, including areas such as mechanical engineering, biophysics, biology and chemistry. The diversity of the participants' backgrounds has given a strong synergy effect that is one of the reasons why the research group within a few years has taken a leading position in the field of pelletization research. This has resulted in presentations at the major conferences within the field, both nationally and internationally (2) (3) (4) (1).

#### **4.1.3 Methods**

Electron- and light-microscopy has been used to investigate the structural changes induced during the pelletization process. The techniques of Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) have been used to study pellet surfaces and bulk material. Novel mechanical methods developed during the ongoing project have been used to produce and test pellets made of straw and other biomass residues. In addition, modelling tools have been used to test the experimental results against the theory.

#### **4.1.4 Collaboration with other research institutions and private companies**

The EFP-project is carried out in collaboration with DONG Energy and Vattenfall A/S. DONG Energy and Vattenfall A/S own together a large pellet factory in Køge, south of Copenhagen. The factory makes it possible to carry out large-scale tests and links the fundamental research at laboratory scale to the large industrial scale. The advanced analyzing techniques are carried out in collaboration with partners at the Norwegian University of Science and Technology (NTNU, Trondheim, Norway) and Risø National Laboratory.

#### 4.1.5 Pellet production

The overall production layout for straw and wood pellets at Køge Biopellet factory is given in Figure 2. As can be seen, the production of straw pellets is simpler than the wood pellet production as the straw does not need drying. The straw is entering the factory as bales which have to be broken down in the straw shredder. From here the straw is transported to the hammer mills where it is comminuted to mm-sized particles. Hereafter the straw is pelletized with the addition of steam and binding agents. The produced pellets are transported to the cooler where the pellets are hardened.

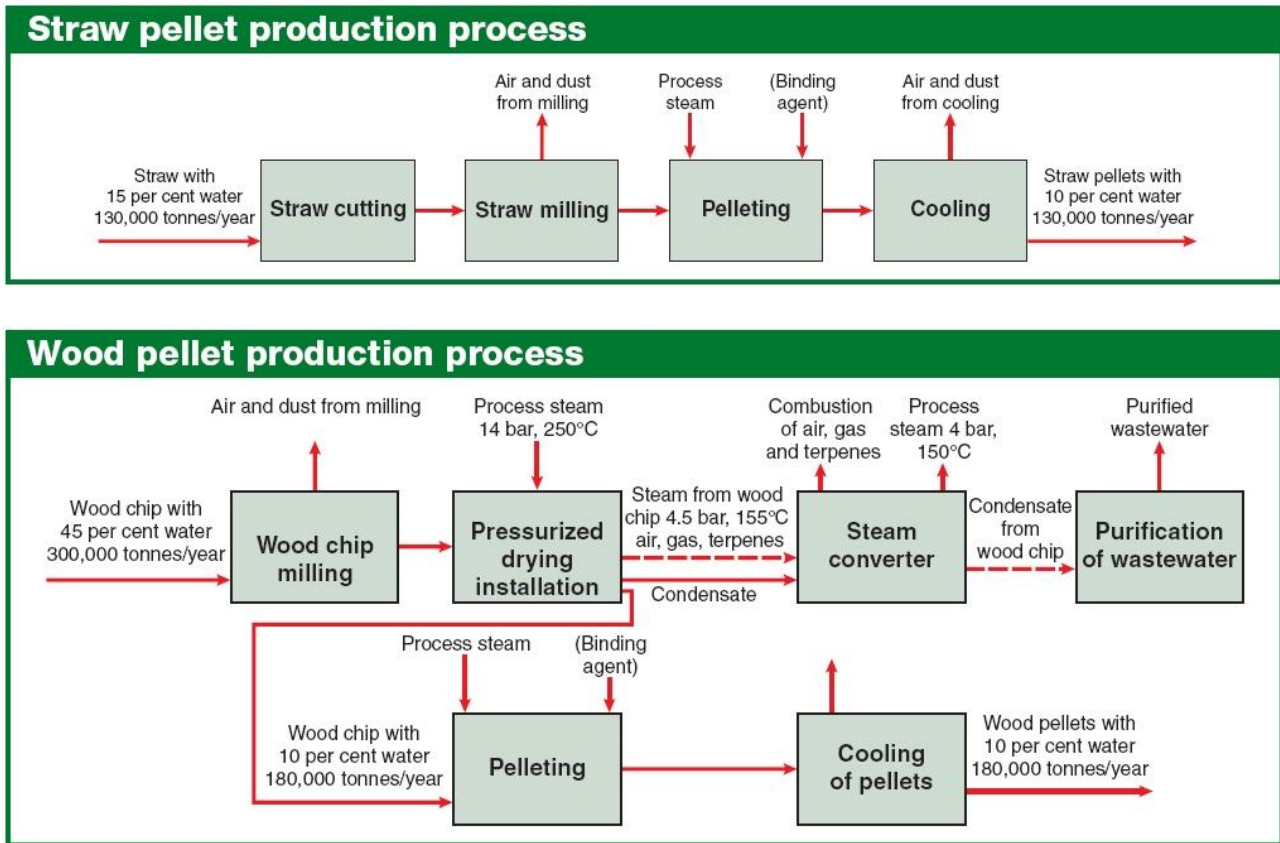


Figure 2 Straw and Wood pellet production process. Figure adapted from (16).

The wood pellet production is more complex as the wood chips need drying before the pelletization. The drying process takes place in a pressurized drying installation with steam from the nearby CHP plant.

#### 4.1.6 How to control the pellet production process

The reason why wood dust is converted into pellets in the channels of the matrix is due to friction forces, which counterbalance the pressure forces exerted by the roller. This mechanism is described in (6). In order to explain the pelletization process two material properties are important to have in mind:

1. If a material is compressed in one direction, it will expand in the two perpendicular directions. Further, if the material, like wood, is orthotropic, the expansion in the two other directions will be independent from each other. When the deformations are confined to the elastic range, the ratio between the applied pressure and the transverse expansion is described by Poisson's ratio. If the material is confined to a matrix channel it is spatially restricted and the potential expansion is converted into a transverse pressure on the channel walls.
2. If the material is compressed over the yield point, it will be permanently restrained in the channel even after the pressure has been removed. This property ensures that the pellets do not fall out when the roller pressure is removed.

In short, the idea is that the pressure of the roller exerts a pressure on the wood particles. In turn, the compressed particles exert a pressure on the channel walls, leading to the establishment of friction forces that hinder the free movement of the particles/pellet in the channel. It is important to realize that the pressure forces are self-reinforcing (i.e., the friction force increases as the pressure force increases). This gives rise to a pressure force that increases exponentially from the outlet to the inlet of the channel.

#### **4.1.7 Raw materials**

The raw materials for the pellet production are characterized by great diversity. Typical sources are sawdust, shavings from dry and debarked wood and decomposed wood chips. In addition, the material originates from different wood species, having different mechanical properties that influence the pelletization properties.

Because the raw material is clean debarked wood, the pellets have very low ash content, usually around 1%. Higher ash contents indicate that the material has not been handled properly and hence contaminated during handling. If the ash is furthermore rich in compounds having low melting point, there is a potential risk of slag formation and corrosion.

## 5 Structure of wood

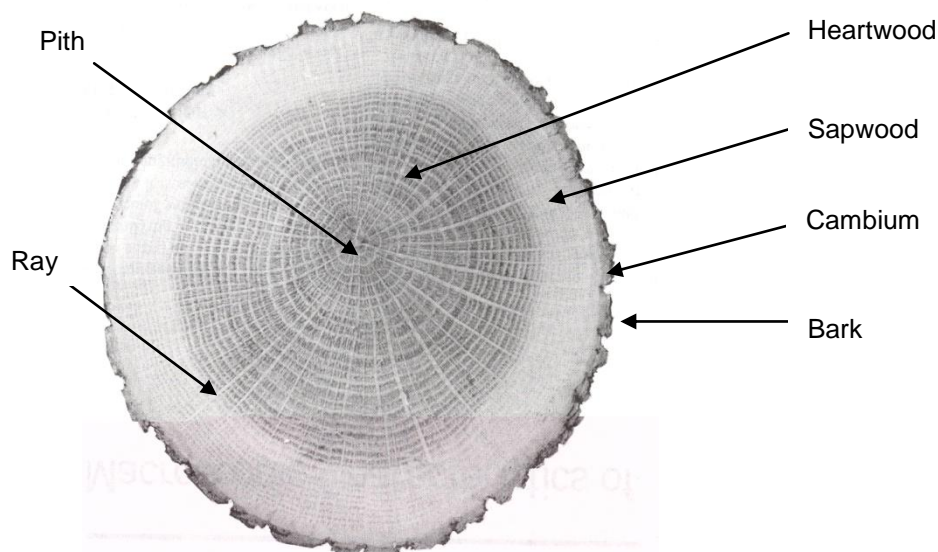


**Figure 3 Wood chips from Junckers Industries. a) Softwood shavings b) Beech (hardwood) c) Pinewood (softwood).**

The raw material for pelletization of wood is typically milled or otherwise processed remains from the wood industry. In Denmark, Junckers Industries manufacturing floor boards, has until recently been supplying ‘Køge biopillefabrik’ with wood raw material.

Figure 3 shows raw materials used for pelletization: sawdust shavings of pine and milled samples of beech and pine, respectively. The sawdust shavings have a very different grain shape from the milled samples. While the former consists of very thin flakes, the latter are needle-like and mixed with dust. Wood is a hierarchical, heterogeneous, composite material and in addition highly anisotropic. In general, wood samples for pelletization originates from various regions in wood and thus have mixed characteristics. The grains generally have a broad size distribution, ranging from dust to cm-large pieces. *A priori* it is to be expected that grain sizes and shapes together with the particular microscopic structure of the grains which depend on wood species and location in the tree trunk, will play an important role in the pelletization process due to the importance of the size of the contact area for adhesion forces and the specific mechanical properties of the wood sample in question. Measurements carried out in our laboratory suggest that the strength of the pellets depends on a complex interplay between particle size and temperature. At high temperature ( $\sim 120$  °C) the pellet strength seems to be less dependent on particle size than at room temperature, where pellets made from larger particles give the highest strength.

## 5.1 Macroscopic structure of wood



**Figure 4 A transverse section cut of an oak trunk. Figure is adapted from (17).**

In a tree trunk there are three main areas (see Figure 4): Pith, xylem and bark. The vascular cambium, a lateral meristem of dividing cells, produces bark or phloem on the outside and sapwood (part of the xylem) on the inside. The bark is divided into two layers with the outer layer serving as a protective layer and the inner bark layer playing a role in transport of sugars. Diluted sap flows through the sapwood – hence the name. The sapwood xylem cells become progressively more dissociated from the cambium as the tree grows and after physical and chemical changes these cells change to coloured heartwood cells, which are not active in water transport. Sapwood and heartwood together form the xylem. The new growth of wood is added to the outside of existing wood, thus the oldest wood is close to the pith. Differences in growth conditions during the year will produce the characteristic concentric bands, the growth rings. The pith (or parenchyma) plays a role in storage and transport of both liquids and gasses. The rays are radial structures from pith to bark allowing transport of nutrients in the transverse direction. Certain species also possess longitudinal resin canals, which in a transverse section appear as small dark or whitish dots.

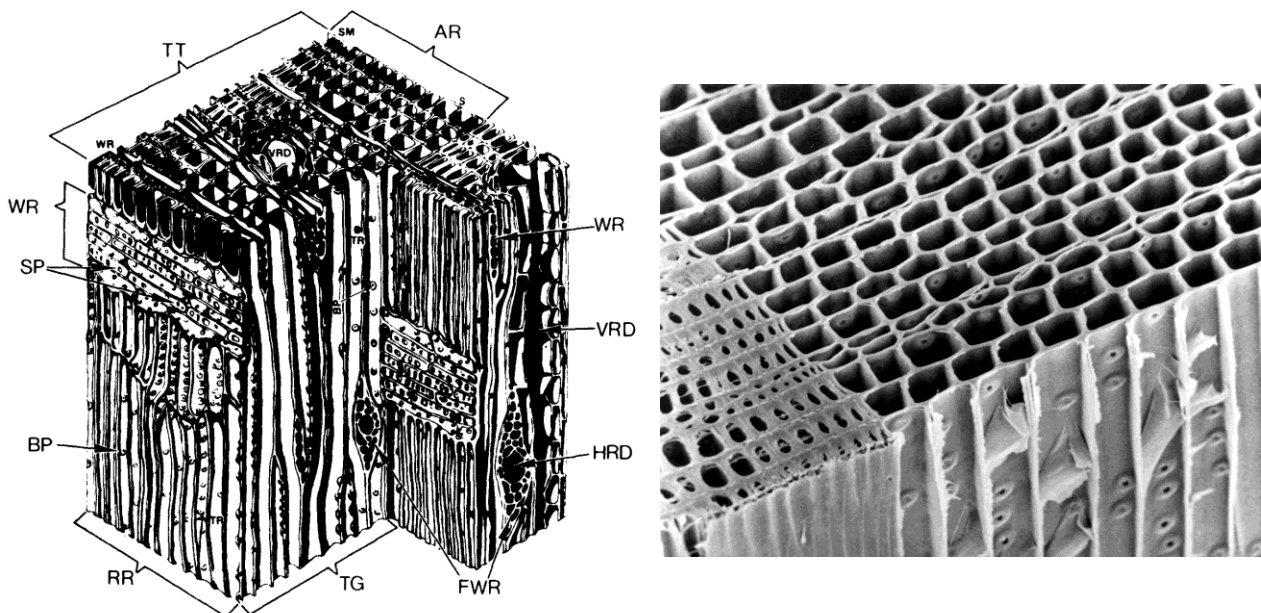
## 5.2 Microscopic structure of wood

Wood is divided into two broad classes – softwood and hardwood. The names are not directly related to the mechanical properties of wood, but refer to botanical characteristics. Softwoods (e.g. Douglas fir, pine and spruce) are cone-bearing, have needle-like leaves and are evergreens, while hardwoods (e.g. oak, beech, ash and birch) are broad-leaved and deciduous (shed the leaves). In botanical terms softwoods are gymnosperms with naked seeds and hardwoods angiosperms with covered seeds.

In both types of wood, cells can be divided into three different groups according to their function as conducting cells, supporting cells or storage cells. The two former types are dead cells with air or fluid filled cavities (lumina).

The cellular structure of softwood is the simpler of the two wood types. The dominating cell type is the tracheid cell. Tracheid cells are rather long tubular cells oriented along the tree trunk with a typical length of about 2-4mm, diameter 10-50  $\mu\text{m}$  (18) (19), i.e. about 100 times longer than wide and with an internal cavity or lumen.

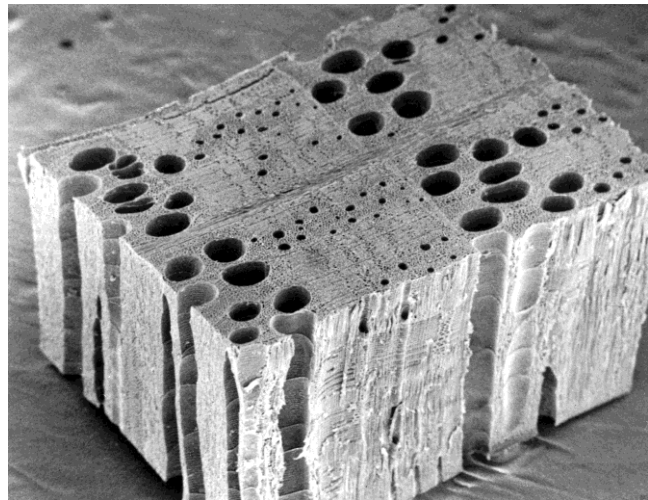
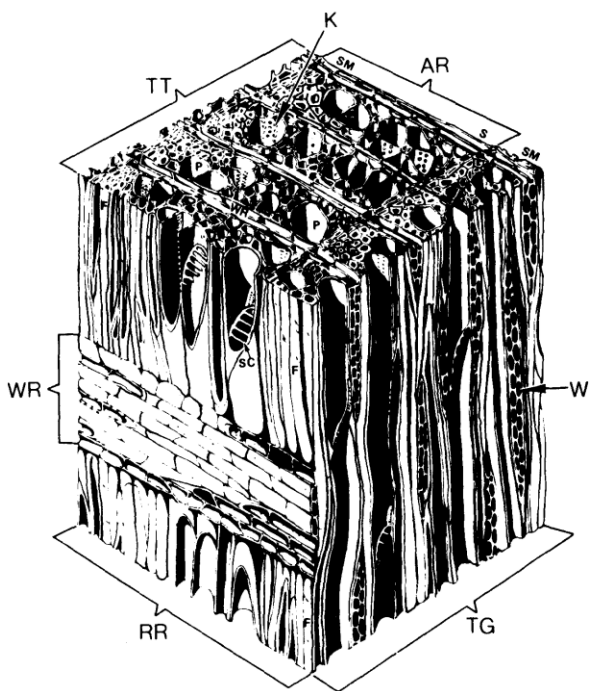
The thickness of earlywood tracheid cell walls is 2 -4  $\mu\text{m}$  and of latewood tracheid cell walls 4-8  $\mu\text{m}$  (19). Earlywood is fast-growing and have thin-walled tracheids with large lumina specialised for fluid conduction. These cells have many pits (valves) in the cell wall in order to control the flow of sap - typically about 200 in earlywood tracheids and 10 – 50 in latewood tracheids (19). Latewood is slowly growing and the tracheids are thick-walled with narrow lumina, have pointed ends and few pits and function as the main support tissue giving the tree its strength. The two types of tracheid cells are shown in Figure 5. 90-95% of the cells in softwoods are tracheids, while ray cells constitute 5-10% (19). Ray cells are radially oriented and are used for transport (ray tracheids) and storage (ray parenchyma, which are small, thin-walled and box-like). The cellular structure is for some species occasionally interrupted by resin channels which can be both longitudinally and radially oriented. These channels allow the flow of resin (Figure 5).



**Figure 5** <http://www.fpl.fs.fed.us/documnts/fplrn/fplrn004.pdf>.

**Cell structure of a softwood.**

**5a) TT – Transverse plane. TR – Tracheid. S – Earlywood cells. SM – Latewood cells. AR – annual ring. WR – Wood ray. FWR – Fusiform wood ray. HRD – Horizontal resin duct. VRD – Vertical resin duct. RR – Radial plane. TG – Tangential plane SP – Simple pit. BP – Bordered pit . 5b) Scanning Electron Micrograph of pine.**

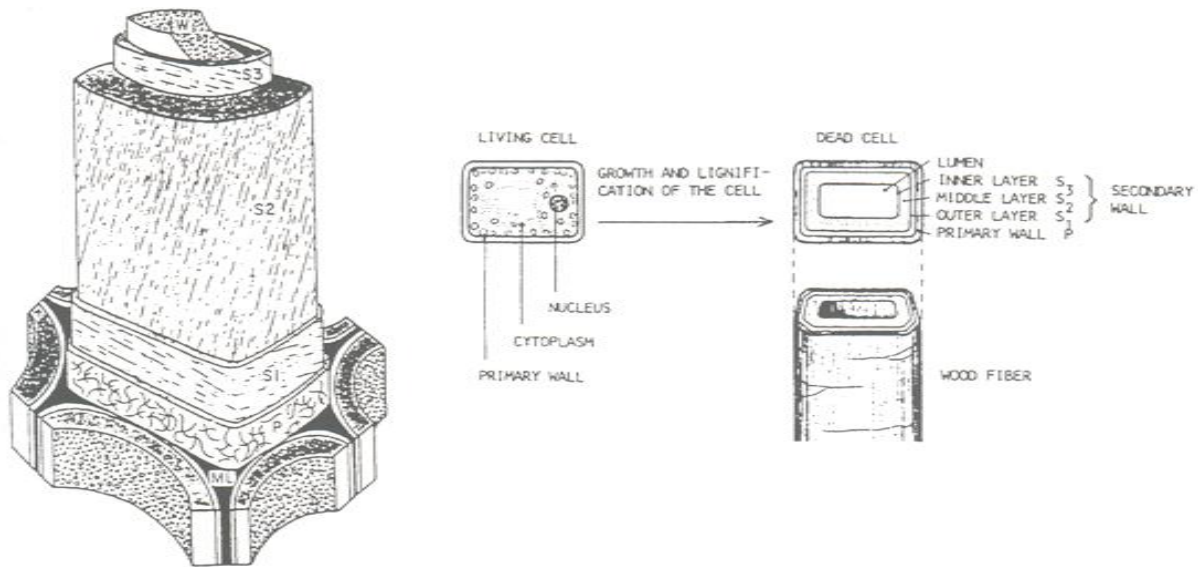


**Figure 6** <http://www.fpl.fs.fed.us/documnts/fplrn/fplrn004.pdf>. Cell structure of a hardwood. 6a) TT – Transverse plane. P – Vessel opening. SC – Vessel with crossbars. F – Wood fiber. K – pits. S – Earlywood cells. SM – Latewood cells. AR – annual ring. WR – Wood ray. RR – Radial plane. TG – Tangential plane. 6b) Scanning Electron Micrograph of oak.

Hardwoods are more heterogeneous in structure than softwoods and different types of cells are responsible for transport and strength. Conduction of fluids takes place via vessels, which are short cells (0.3 – 0.6 mm long and diameter up to 0.4 mm (19)) with open ends connected to other vessels to form long (~ 10 m) open passages in the wood (Figure 6). Vessel cells account for 6 – 50% of the wood volume. The main supporting cells are fibers which are typically thick-walled (depending on species) needle-shaped cells about 1 mm long with pointed and closed ends. Fibers account for 25 – 75 % of the wood volume. In hardwood radially running ray cells are exclusively parenchyma cells for storage and these account for 5 – 30% of the wood volume.



### 5.3 Structure of the cell wall



**Figure 7 Simplified structure of a wooden cell and the development of the living cell to a wood fiber. ML – Middle lamella. P – Primary wall. W – Warty layer. S<sub>1</sub> – outer layer of the secondary wall. S<sub>2</sub> – middle layer of the secondary wall. S<sub>3</sub> – inner layer of the secondary wall. Figure adapted from (18). Figures originally from H. Bucher (1965) *Hespa. Mitt.* 15, 1 and W.A. Coté (1967) *Wood ultrastructure*, University of Washington Press.**

All the cells in wood are cemented together into tissue by a thin layer, the middle lamella, which has a high content of lignin and pectin, but no cellulose (ML in Figure 7). The walls in the wood cells are built up of cellulose microfibrils with a diameter in the order of a few nanometers and with different orientations in different layers. The cellulose fibrils are embedded in a matrix of hemicelluloses and lignin, where hydrophilic hemicelluloses bind to the fibrils and thus form a gel-like matrix around the fibers (20).

The microfibrils are wound around the hollow wood cells with an angle relative to the cell long axis called the microfibril angle. The value of this angle varies from 0 to 50° (21), depending on species, growth conditions, location in the wood specimen and location in the cell wall. The microfibrils are semi-crystalline bundles of cellulose molecules held together by hydrogen bonds. Each cellulose molecule is a chain of about 10000 glucose units linked together (19).

The primary wall (primary referring to the time of formation) is composed of loosely aggregated, irregularly arranged cellulose microfibrils, which allow stretching of the cell during growth. When the cell matures, a secondary wall with three layers appear inside the primary wall (see Figure 7): S<sub>1</sub> and S<sub>3</sub>, the outer and the inner secondary layer, respectively, are thin (S<sub>1</sub> ~ 0.2 – 0.3 µm and S<sub>3</sub> ~ 0.1 µm), while the middle wall layer, S<sub>2</sub>, is relatively thick (1 µm (earlywood) and 5 µm (latewood)). The three secondary layers are distinguished by different microfibril orientations, but the orientation within each sublayer is reasonably well-defined. The cell lumen might be lined with a warty layer (W in Figure 7), which is laid down just prior to cell death, covering the entire S<sub>3</sub> layer (22).

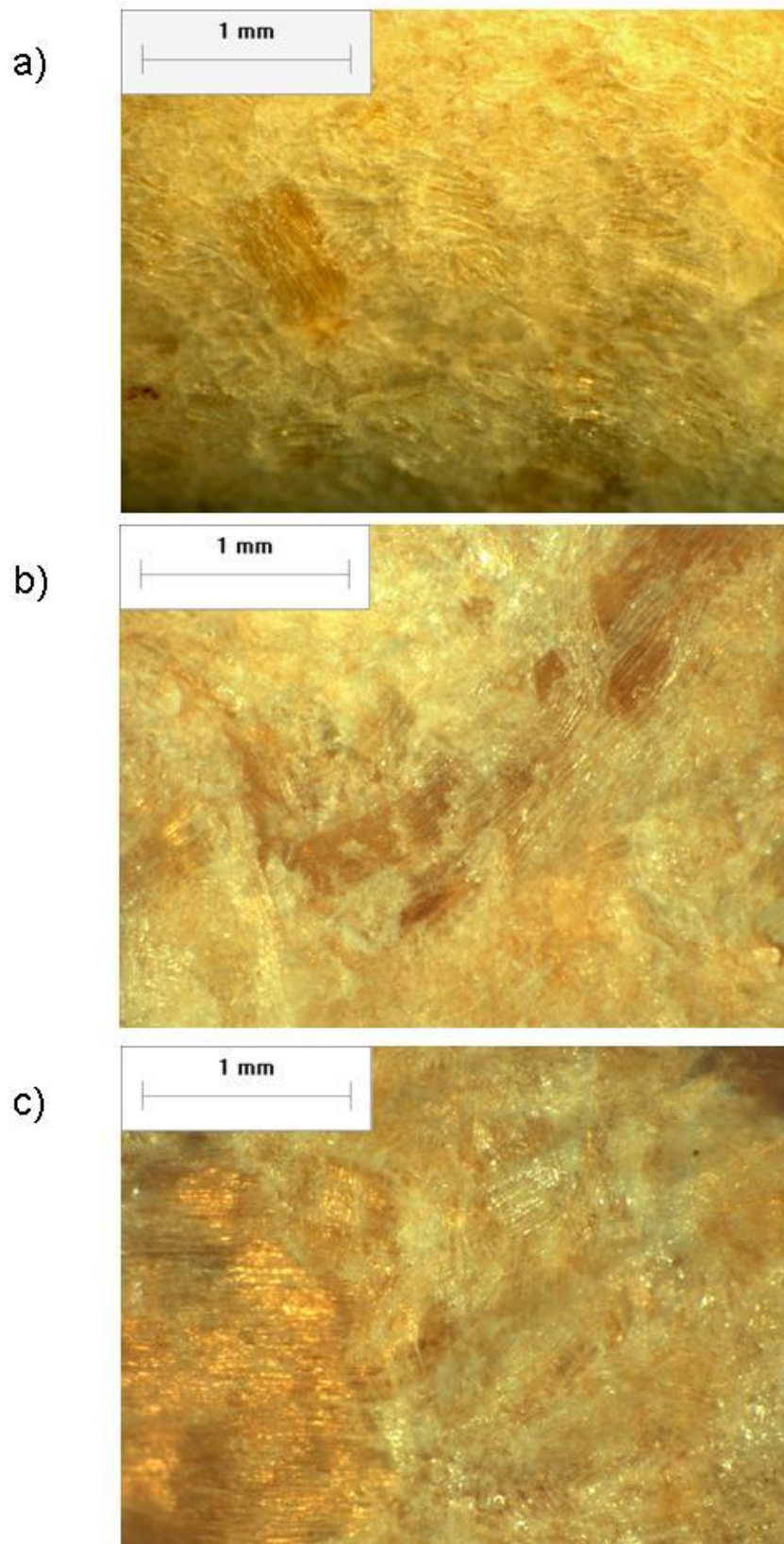
The thick middle layer,  $S_2$ , plays the dominating role in determining the mechanical properties of wood since it takes up large volume fractions of the wood (~ up to 80%) (23). However, the difference in microfibril angle between the different layers means that  $S_2$  with a relatively steep angle gives tensile resistance, while  $S_1$  and  $S_3$  with a large angle between microfibrils and cell axis contributes to compression resistance (18).

#### 5.4 Light microscopy

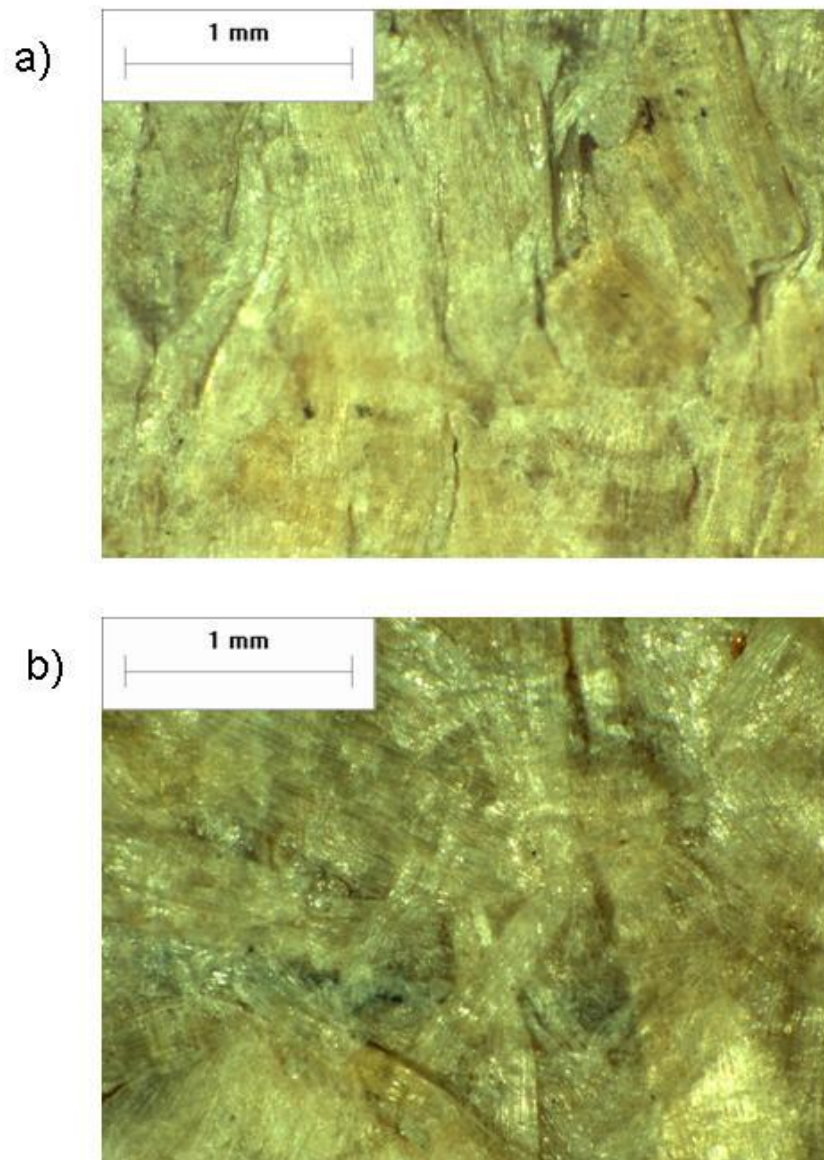
In Figure 8 are shown light microscopy pictures of pressed pellets made of softwood shavings from Junckers Industries (x32 and eyepiece x10). Figure 8a shows a pellet from the ring matrix pelletizing machine. Three images are superimposed and the cross-section is from the outer surface of the pill. Individual tracheids can clearly be distinguished. Just from looking at the outer surface of the pill which has been pressed against the matrix channel surface, the pellet appears shiny as if covered by a waxy layer. However, our results from both chemical analysis and microscopy shows that the surface appears shiny not because of any segregation, but because the surface is mirroring the smooth inner channel surface. This is possible because of the high pressure and friction during pressing which ‘melts’ the surface of the pill allowing it to be moulded in the press channel.

In Figure 8b four images are superimposed and the resulting image shows the fractured surface of a pill. The lower surface of the fractured pill is concave, reflecting the ease with which material across the pellet is being transported through the channel (material adjacent to the channel walls is lacking material in the center behind due to friction). Long parallel bands of 5-10 tracheids are very clearly seen in this image. Finally Figure 8c also shows four superimposed images of the fractured surface.

Figure 9 shows images of a pellet made in the single pelletizer from common spruce (softwood). Three images are superimposed. Figure 9a is an image of the side of the pellet, while Figure 9b shows the top surface of the pellet pressed against the piston. In both cases the tracheids of the needle shaped raw material are clearly distinguished. Similarly the individual needles are still discernible, in spite of the high pressure and temperature during pressing (~1000 bar and ~120°C). The image from the top surface shows needles with all possible tracheid orientation (although needles appear to be predominantly oriented parallel to the top surface). The needles touching the inner channel surface appear to be oriented with parallel tracheids to a higher degree.



**Figure 8 . Light microscopy of softwood pellets. a) Outer surface of the pellet. b) Fractured surface. c) Fractured surface.**



**Figure 9** Light microscopy common spruce. a) Side of the pellet. b) Upper surface of the pellet.

Figure 10 shows a 8 mm diameter commercial pellet broken in two, where this needle orientation is seen.



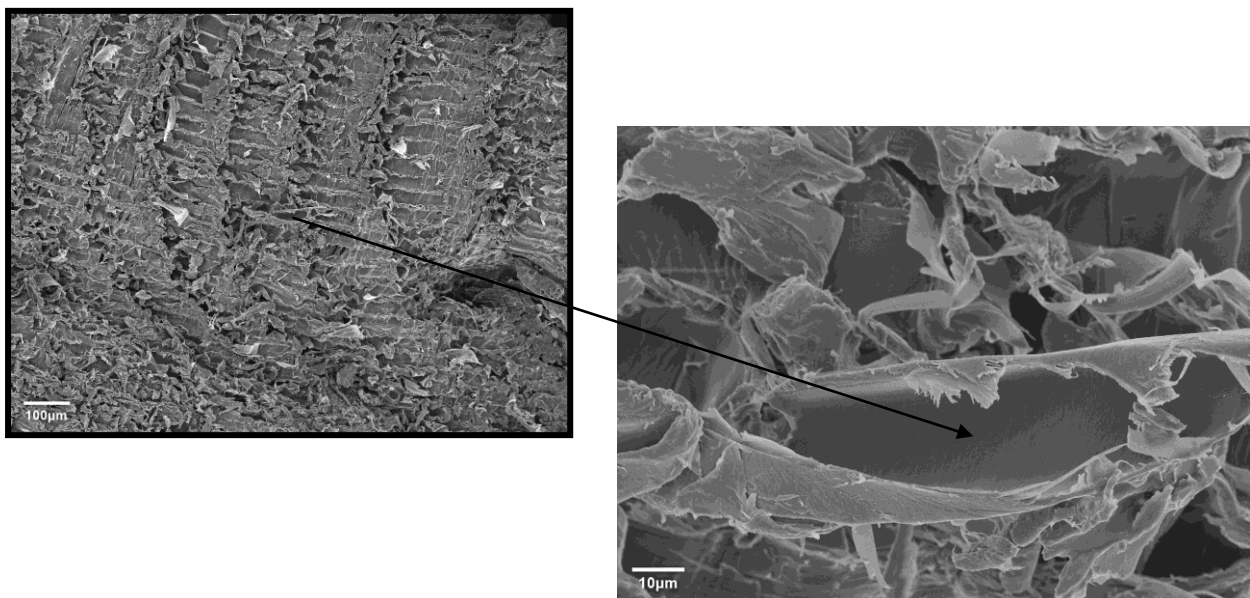
**Figure 10 Commercial pellet broken in two.**

### **5.5 Electron microscopy**

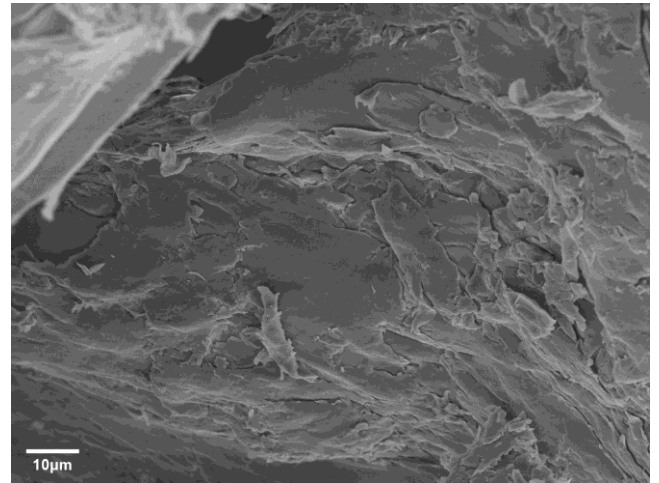
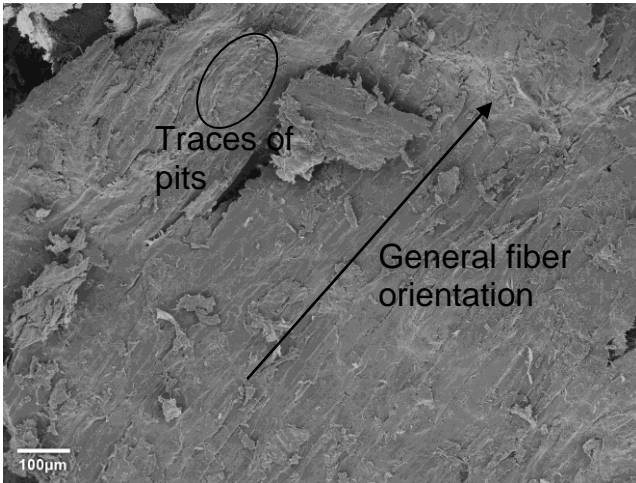
Scanning Electron Microscopy (SEM) was performed using a Jeol Scanning Microscope (JSM 6335F). The pellets to be imaged were sawn with a coping saw and a thin platinum layer (platinum 80%, palladium 20%) was deposited on the surface by evaporation before investigating the sample with SEM.

Figure 11 shows softwood shavings where the tracheids are clearly seen. In the enlargement a tracheid cut through is seen and the inner part of the cell wall is exposed. In addition, pits can also be distinguished.

Figure 12 shows the fractured surface of a pellet pressed from the raw material shown in Figure 11. Not surprisingly, the material appears more homogeneous with fewer distinguishing features after pressing, however traces of cell anatomical details can still be seen in correspondence with the fact that the pressing does not reduce the pellet density to the density of the cell wall material, but to about 75% of the cell wall density.



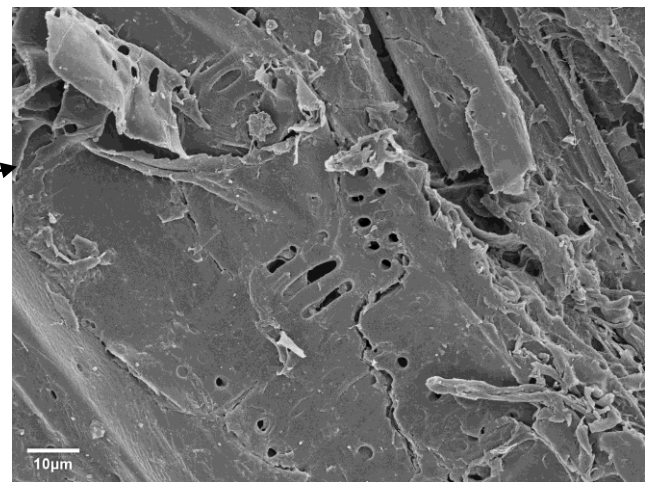
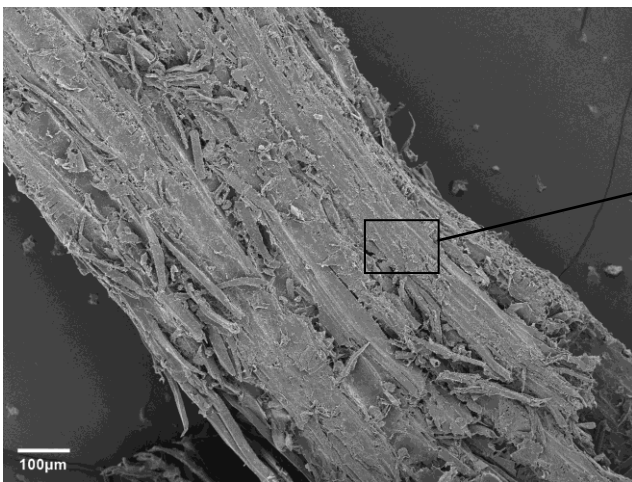
**Figure 11 Softwood shaving (*Pinus sylvestris*).**



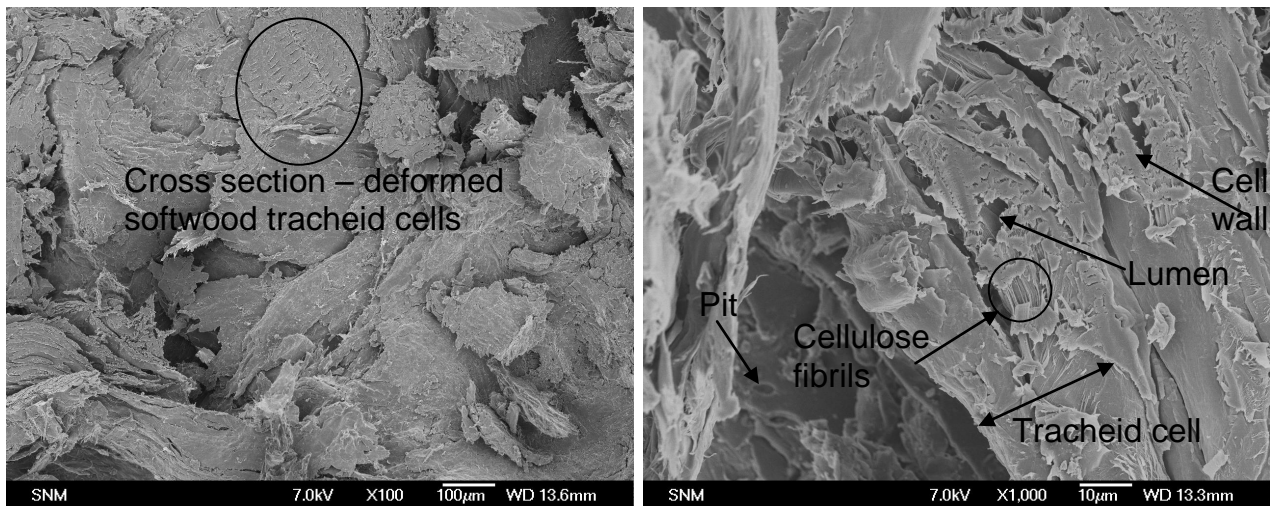
**Figure 12 Fractured surface of softwood pellet.**

Figure 13 shows beech raw material from Junckers industries. Individual fibers are clearly seen as well as pits and cell wall perforations in the large scale image.

Figure 14 shows the fractured surface of a pellet made from 60% softwood and 40% beech. On the large magnification picture a cell with cellulose fibrils is seen. Deformed lumina are seen, but a surprisingly large fraction of “open” lumina are present, considering the large pressures in the pelletizing process.



**Figure 13 Beech raw material.**



**Figure 14 Fractured pellet surface – 60% softwood/40% Hardwood.**

Compared to the mixed softwood/beech pellet (Figure 14), the softwood pellets (Figure 12) appear in general more homogeneous and 'smooth'.

As demonstrated in this section, the structure of wood is complex and hierarchical, thus allowing for the specific mechanical properties giving wood its unique characteristics as a construction material. The presence of long tubular cells is important in modelling the behaviour of wood raw material in a channel press. A surprising degree of organized structure is preserved in the pressed pellets thus giving the pellet an overall density lower than the density of the cell wall material.

## 6 What makes a pellet stick together?

Wood is a highly complex composite material with a hierarchical structure as described in the previous section. The chemical composition of wood is typically more than 90% biopolymers: Cellulose, hemicellulose and lignin. A popular analogy is to compare wood with reinforced concrete with lignin corresponding to the concrete and cellulose comprising the reinforcement while hemicellulose is a filler. The reinforcement gives added strength by taking up tension stresses, while the lignin bulk takes up compression stresses. When passing through the pellet press, wood chips are subject to high pressures (~1000 bar) and the density of each wood chip is increased from typically ~700 kg/m<sup>3</sup> (Beech 15% moisture) to ~1200 kg/m<sup>3</sup>. The density of the cell wall material is about 1560 kg/m<sup>3</sup>, i.e. even pressed pills contain cavities. An important quality of the resulting wood pellet is the strengths in terms of the durability (see chapter 8 for standards). In order to achieve a pellet with a suitable strength the wood chips must be bonded together during the pelletization process. Such bonding can take place either by chemical or mechanical bonding. Chemical bonding involves the biopolymers, where lignin especially is thought to have a 'gluing effect' (18) and in this context the temperature during the pelletization process is an important parameter. The water content of the chips and the ability to form hydrogen bonds between wood chips is very likely highly important as described later in this chapter. Finally the chip might also be held together by mechanical strain produced by squeezing the wood chips together in the pellet press. The concept of a 'jamming transition' from the theory of granular material might be a useful concept in this

context as described later in this chapter. The size and shape of the wood chips are important for chemical bonding, e.g. in terms of the size of the contact surface area between wood chips where chemical bonds can be formed relative to the wood chip bulk which is not expected to take part in the bonding. The size and shape of the wood chips are also of crucial importance for the distribution of stresses through contact points and thus also important for mechanical bonding. Thus many parameters will influence the quality of the final wood pellet: The chemical composition, the water content and the specific mechanical properties (related to wood species) of the wood chips, the temperature and pressure during the pelletization process and the size and shape of the wood chips.

## 6.1 Biopolymer binding

The main chemical constituents of wood are cellulose, lignin and hemicellulose.

### 6.1.1 Cellulose

Typically 40 – 45 % of the dry wood weight is cellulose (19). Cellulose is a polysaccharide linking typically several thousand glucose rings together (see Figure 15). Cellulose chains are straight extended rods and they form easily fibers organized in a hierarchical structure: elementary fibrils, microfibrils and fibers. The microfibrils are bundles of elementary fibers aggregated together and in these microfibrils, highly ordered crystalline regions alternate with less ordered, amorphous regions. The inter- and intramolecular bonds holding the fibers and the fiberbundles together are hydrogen bonds. Due to the fibrous structure and strong hydrogenbonds within the fibers, cellulose is insoluble in most solvents.

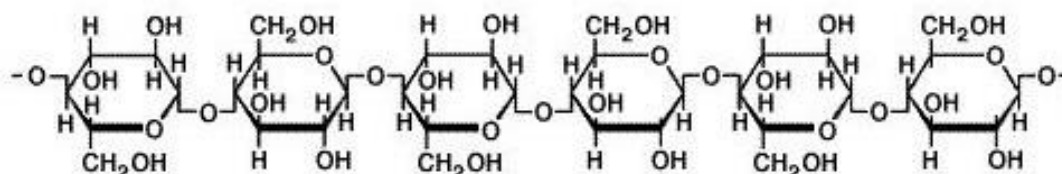
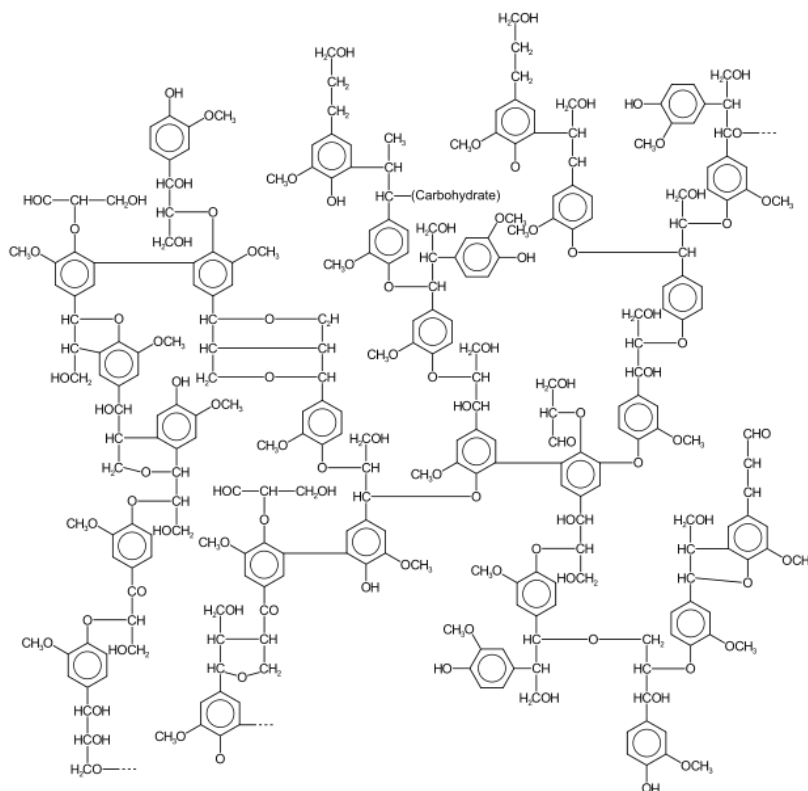


Figure 15 Part of cellulose molecular chain. <http://da.wikipedia.org/wiki/Cellulose>

### 6.1.2 Lignin

Typically 20 – 30 % of the dry wood weight is lignin (19), the values somewhat higher for softwoods than for hardwoods. The highly ramified structure of the lignin molecule is a random repetition of different substructures based on polyphenol (see Figure 16). Contrary to cellulose, lignin is amorphous, relatively hydrophobic and have an aromatic character. Lignin is inhomogenously distributed in the cell wall (e.g. 70-80% of the midlamellae consist of lignin).





**Figure 16 Part of a lignin polymer elucidating the random character.**  
[http://en.wikipedia.org/wiki/Image:Lignin\\_structure.svg](http://en.wikipedia.org/wiki/Image:Lignin_structure.svg)

### 6.1.3 Hemicellulose

Hemicelluloses are heterogeneous polysaccharides (coupling of pentosanes and hexosanes) typically with a lower molecular weight than cellulose and constituting typically 20 – 30 % of the dry weight in wood (19). Structure and composition of softwood hemicelluloses are distinct from hardwood hemicelluloses and likewise for hemicelluloses from various parts of the tree. Hemicellulose is a branched polymer, amorphous and hydrophilic.

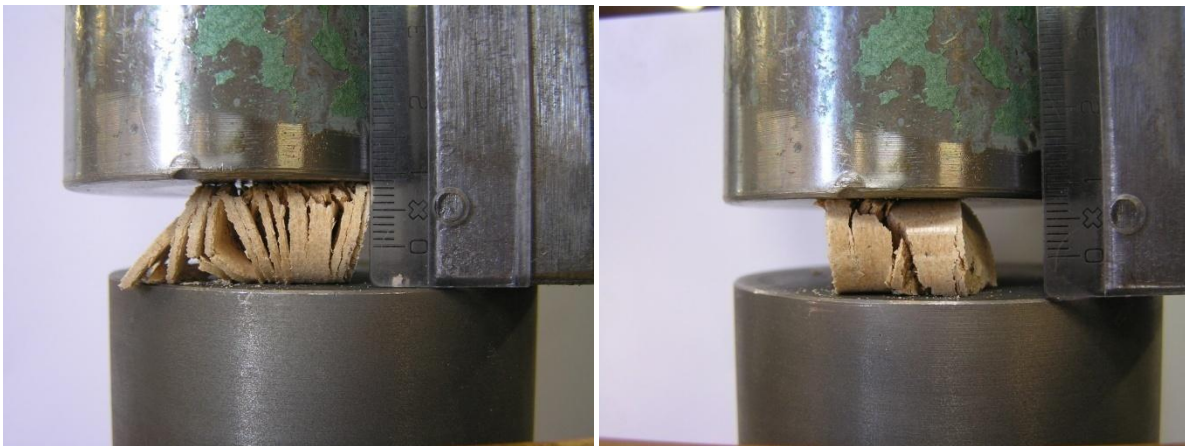
## 6.2 The glass transition

Amorphous polymers (and other types of glass-forming liquids) show characteristic viscoelastic behaviour as function of temperature with the glass-transition temperature,  $T_g$ , separating low-temperature behaviour from high-temperature behaviour. At temperatures below the transition, the polymer is stiff and glassy, while it exhibits rubber-like elasticity as a result of chain entanglement above the transition. The polymer will eventually flow when the temperature is high enough, provided it is not cross-linked. Experimentally, the glass transition can be observed as e.g. a change in the elastic moduli or in the heat capacity. The exact value of the glass transition temperature depends on the method of determination, the degree of crystallinity (for cellulose), the water content and time (frequency). A typical value for cellulose is 230°C (18) and for lignin in water-saturated wood the glass transition occurred over the approximate temperature interval 60-90°C (24). Using a dynamic mechanical thermal analyzer, it was found that at 30% moisture content the  $T_g$  of *in situ* lignin is 60°C and the  $T_g$  of *in situ* hemicelluloses is - 10 ° C at 1 Hz (25). These  $T_g$ s are heavily dependent on both moisture content and measurement frequency.

It is thus plausible that wood hemicelluloses is above the glass transition temperature for all practical purposes relevant to pelletizing, while the lignin glass transition is in the relevant range of working temperatures. I.e., lignin might be both above and below the glass transition, depending on the exact pelletizing conditions. Usually a temperature of  $\sim 120^\circ\text{C}$  is achieved in the pellet mill. It is unlikely that lignin will flow above  $T_g$ , since lignin *in situ* in wood constitutes a cross-linked polymer network also associating with the other biopolymers in the cell wall (18), unless the temperature is high enough for thermal degradation of lignin to take place. However, when the matrix in which the cellulose fibers are embedded become soft, the polymer chains become more mobile and bonding between neighbouring wood chips can occur by chemical bonding (hydrogen bonding) or formation of polymer entanglements by the matrix polymers. At such high temperatures that cellulose is above the glass transition, also cellulose fiber entanglements can contribute to the bonding of wood chips. However, temperatures above  $\sim 250^\circ\text{C}$  are not very frequently encountered during standard working conditions and at such high temperatures, chemical degradation of the wood constituents must also be considered.

### 6.3 Wood welding

Recently, it was reported that applying mechanical friction under pressure will weld together two pieces of solid wood (26) (27). The wood is heated due to the mechanical friction and lignin and hemicelluloses start to flow (these compounds gets permanently altered in the welding zone (26) (28)). In a simplified picture, wood fibres are then released which can subsequently become entangled and form a bond which is 'frozen in' when the wood is cooled down after the process. In the case of pellet pressing, no friction is applied between the wood chips to be bonded, but this might be compensated by the applied pressure being much higher than for wood welding. One might therefore speculate that similar bonding processes are relevant for pellet pressing. Indeed we have found that two cm-large flat pieces of wood are bonded together when pressed together in the single-pellet press.



**Figure 17 Strength test of pellets pressed at  $20^\circ\text{C}$  (left) and at  $120^\circ\text{C}$  (right).**

Figure 17 shows the relation between press temperature and pellet strength. At  $20^\circ\text{C}$  the pellet will predominantly break up into the original discs, from which it is made. At higher temperature ( $120^\circ\text{C}$ ) the chemical binding between the discs is so strong that the fracture is more irregular and not confined to the boundary between the individual discs.

## 6.4 Water binding in wood

The water content of the raw wood chips for pellet pressing is an important parameter in determining the pelletizing properties of the raw material.

One observation with a single pellet press to illustrate the point, concerns pressing of two whole pieces (cm-sized) of wood, inspired by recent publications of ‘friction-welding’ of wood as described in the previous section. Dried wood will not stick together permanently after pressing, while wood with a certain water content forms what looks like a homogeneous piece of wood, even if the wooden pieces have been previously pressed (a common observation is the difficulty of pressing pellets of previously pressed material – only about 10% recycled material can be accepted).

Moisture content is a very important parameter in the timber and wood industry (e.g. furniture manufacturing) and there is a vast literature concerning moisture-wood relations on a macroscopic ‘timber’ scale. Regarding pelletizing and binding in wood pellets, we are concerned with molecular interactions between water and specific wood biopolymers. The literature concerning these aspects is more limited.

Water in wood is contained both in voids as free liquid water, as water vapour in lumina and cavities and as water chemically bound to biopolymers in the cell walls. The moisture content is defined as the relative difference in weight between the ‘fresh’ wet piece of wood,  $W_{wet}$  and the weight after drying the piece in an oven (typically at 105°C (29)),  $W_{dry}$ :

$$\text{Moisture content} = \frac{W_{wet} - W_{dry}}{W_{dry}} \cdot 100\%$$

Moisture content in freshly sawn wood varies from species to species and between different locations in a tree. Typical average numbers are American beech 55% (heartwood) - 72% (sapwood), California oak 76% (heartwood) – 75% (sapwood), noble fir 34% (heartwood) – 115% (sapwood), Sitka spruce 41% (heartwood) – 142% (sapwood) (30).

Control over the moisture content in wood requires control of air humidity and temperature under storage. The fibre saturation point is defined as the moisture content with no free water present in the wood sample, but with full saturation with regard to bound water. Loss of water below the fibre saturation point leads to shrinking and a change in the mechanical properties (the modulus of elasticity increases). After a summer in a ventilated shed, a stack of lumber has typically a water content of 20-30%, corresponding roughly to the fibre saturation point (25-35%). The required maximum water content in wood for burning depends on the degree of sophistication in design of the boiler. Commercial wood pellets typically have a water content of 8%-10%, i.e. the raw material for pelletizing has to be dried. Pellets cannot be pressed if the water content is more than 12-15% and pressed pellets will disintegrate if the water content increases above this level.

In practice, the fibre saturation point is not well defined, but depends on sample inhomogeneity, drying method and the particular property of wood under consideration for

appreciable changes when changing the moisture content below the fibre saturation point, e.g. volume, elastic modulus, electrical resistivity (31). The moisture content of wood below the fibre saturation point is a function of both relative humidity and temperature of the surrounding air.

Free water in the wood cell lumina is contained by capillary forces, but not chemically bound. When free water is removed, the physical properties of wood stay largely constant.

Bound water is taking part in a hydrogen bond network with the macromolecular cell wall components, cellulose, hemicellulose and lignin. All three types of macromolecular cellular building material have free hydroxyl groups (OH groups), which can hydrogen bond both with each other and with water. As a result of the binding of water to the cell wall, the cells swell and the mechanical properties of the material are altered.

A hydrogen bond is an attractive electromagnetic interaction between two partial electrical charges of opposite polarity – a partial positive charge  $\delta^+$  on hydrogen and a partial negative charge  $\delta^-$  on oxygen (in the present case). Water is a highly polar molecule where the electron cloud forming the bond between hydrogen and oxygen is strongly polarised due to the strong electronegativity of the oxygen lone pairs (filled molecular 2p-orbitals). The resulting relatively large charge density on the small hydrogen molecule can interact with an oxygen lone pair on a neighbouring water molecule likewise with a relatively large charge density, but of opposite charge, thus forming a hydrogen bond. Each water molecule has two hydrogen atoms and two oxygen lone pairs thus enabling a single water molecule to participate in four hydrogen bonds to four neighbouring water molecules. In bulk liquid water a hydrogen bond network is thus formed throughout, resulting in the very specific properties of liquid water. A hydrogen bond is a strong intermolecular interaction, but about 10 times weaker than a covalent bond. It should be noted that a detailed understanding of the hydrogen bond requires a full quantum mechanical model.

The hydroxyl groups on the cell wall macromolecules in wood can also participate in hydrogen bonding, either to neighbouring macromolecules or to adsorbed water. The surface of cellulose polymer chains is densely packed with hydroxyl groups (three in each glucose unit). Depending on steric factors the OH-groups of cellulose molecules are able to form both intramolecular linkages and intermolecular linkages. The intramolecular linkages occur between OH-groups within the same cellulose chain and results in an increased stiffness of the chain. The intermolecular linkages between neighbouring chains hold together the microfibrils in crystalline cellulose. When water is added, the water molecules can penetrate into amorphous regions inbetween the ordered microfibrils. As a result, intermolecular cellulose hydrogen bonds break and hydrogen bonds are formed between cellulose and water instead, these last bonds being the strongest and thus most energetic favourable (32). The cellulose network thus swells and softens. Since the microfibrils are less strongly bonded to each other, they are easier to untangle and stretch, i.e. the stiffness of the wood decreases. Swelling with water also leads to fewer cellulose microfibrils per unit area and thus a decreased strength of the wood.

In contrast to cellulose, hemi-cellulose and lignin are amorphous throughout the wood. Of the three main macromolecules in wood, lignin has fewest hydroxyl groups to bind water. Accordingly, lignin has the lowest affinity for water, while hemi-cellulose has an even higher

water binding capacity than cellulose (33). The amount of hydrogen bonding between cell wall macromolecules and water is in fact so large that a gel is formed, i.e. cell wall material and bound water can be considered to be a single phase. Accordingly, cellulose is not soluble in water.

The chemical composition of softwood lignin and hardwood lignin is not identical and as a result the glass transition temperature of hardwood lignin is lower than that of softwood lignin. In one study of lignin glass transition temperature ( $T_g$ ) (34), a softwood  $T_g$  of 119°C and a hardwood  $T_g$  of 93°C was found for isolated lignin, however it should be kept in mind that modifications of the lignin properties cannot be avoided during isolation. In this study the higher  $T_g$  observed for softwood lignin is attributed to intermolecular hydrogen bonding.

## 6.5 Jamming in Granular Materials

In the model (6) describing the pelletization process, the raw material is basically treated as a bulk material characterized by certain materials parameters, e.g. Poisson's ratio and the sliding friction coefficient. Wood is an orthotropic material and it is assumed in the model that all fibres align perpendicular to the long direction of the press channel, i.e. the relevant Poisson's ratio in the model is  $\nu_{RL}$  = longitudinal strain/radial strain. The pellet produced is compressed against a back-pressure obtained due to friction.

One question arising is 'what holds the produced pellet together once the back-pressure is released?' Chemical bonding, e.g. hydrogenbonding and possibly polymer entanglements are of importance in this respect as described in the previous section. It might however be useful to gain qualitative insight into mechanical mechanisms holding the pressed pellet together by appealing to concepts from the physics of granular materials.

Examples of granular materials are diverse and plenty: corn in a silo, sand on the beach, powders and pills in the pharmaceutical industry, coffee beans in a hopper and coal in a hopper car. A granular material is made up of large ( $\sim\mu\text{m}$ ), solid objects which interact by dissipative, contact interactions, e.g. by friction and inelastic collisions. The requirement of large objects means that thermal fluctuations can be neglected. Contrary to the basic assumption for granular matter, pelletizing raw material interacts also via cohesive forces (e.g. hydrogen bonds) and the wood fibres do deform when pressed together.

Granular materials have unusual load-bearing properties. A well-documented, but not well understood phenomenon in granular materials is *the jamming transition*, a non-equilibrium transition from a fluidlike to a solidlike state. Jamming is 'a state which emerges when a many-body system is blocked in a configuration far from equilibrium, from which it takes too long a time to relax for the timescale to be a measurable quantity' (35). Jamming has been observed in many different systems, both granular materials and emulsions, colloidal suspensions and structural glasses. The jamming mechanisms for these different systems are however very diverse. The jamming transition is a dynamical arrest which occurs when the constituent objects of the system are in close contact with one another and the transition is currently a "hot topic" in physics.

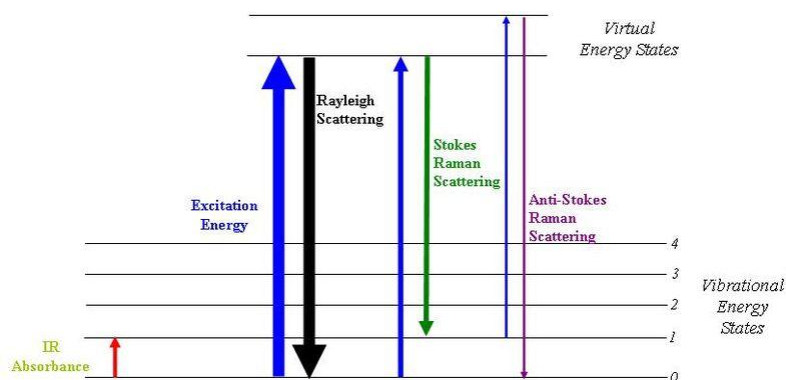
## 7 Chemical characterisation of pellet materials

### 7.1 Introduction

The purpose of the project work involving the Polymer Department at Risø National Laboratory was to determine whether chemical factors could contribute to the quality of compressed biomass fuel pellets. Previous studies have examined the physics of the briquetting process (36) but have generally not addressed chemical issues.

In order to examine chemical changes occurring as a result of the pelletising process, we adopted two instrumental techniques that we considered suitable for analysis of pellet surfaces or bulk material. These techniques were Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

Raman spectroscopy is complementary to infra-red spectroscopy and has the advantage in terms of biological materials that water does not absorb very strongly. Raman spectroscopy relies on the fact that although most light striking a material is scattered elastically (Rayleigh scattering), there are a small number of photons (approximately 1 in  $10^7$ ) that are scattered at frequencies that are different from and usually lower than the frequency of the incident light (Stokes Raman scattering). This is known as the Raman effect (Figure 18) and occurs when the incident light interacts with the electric dipole of the molecules in question.



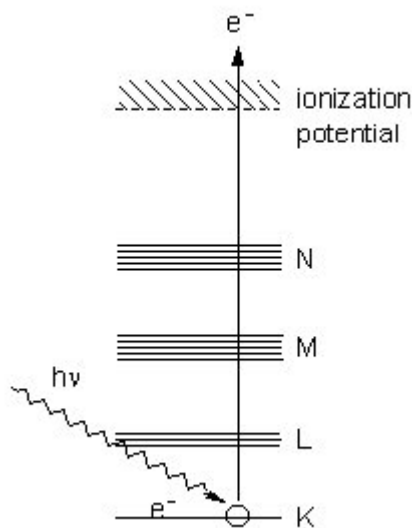
**Figure 18: Schematic of the Raman effect.**

Raman spectra of organic molecules usually occur in the range  $500\text{-}2000\text{ cm}^{-1}$  with peaks expressed in terms of Raman shift, which is the difference in wavelength between the incident laser and the inelastically scattered radiation.

There has already been a significant amount of research in which Raman spectroscopy has been applied to investigations on wood and other forms of biomass. Österberg *et al.* (37) studied extractives on the surface of wood through a combination of Raman spectroscopy and atomic force microscopy (AFM). The authors stated that this was the first case in which unambiguous proof of the chemical nature of different morphological regions in an AFM phase contrast image had been obtained. The authors also claimed that their paper was the

first published work in which wood extractives in pulp and paper samples had been studied using Raman spectroscopy. Other authors have however used Raman to examine extractives in wood and lignin in pulp and paper e.g., (38) and (39). A recent review (40) has also covered the application of Raman microscopy and Raman imaging in plant research

XPS is a widely used instrumental method for analysing the chemical composition of the top 10 nm of material surfaces. Essentially, the technique involves bombarding a sample surface with X-rays under high vacuum and capturing the emitted photoelectrons using a suitable detector. Photoelectrons are emitted at energy levels (binding energies in eV) that are characteristic of transitions within each specific element. Consequently, most elements, with the exception of the lightest (hydrogen, helium, lithium and beryllium) can be detected using XPS. The intensity of the emitted photoelectrons can be used to determine the elemental composition of material surfaces in terms of atom % with a typical accuracy of +/- 10%.



**Figure 19 Schematic of the principles of XPS.**

The binding energy for a particular element can be determined using the equation shown below,

$$E_k = h\nu - E_b - E_w$$

in which  $E_k$  is the kinetic energy of the emitted photoelectrons,  $E_b$  is the characteristic electron binding energy,  $E_w$  is the work function of the spectrometer and  $h\nu$  is the energy of the XPS X-ray radiation.

There are a number of recent studies in which XPS has been used to characterise the surface of wood and some that have specifically dealt with the effects of heat treatment or carbonization (41) (42) (43).

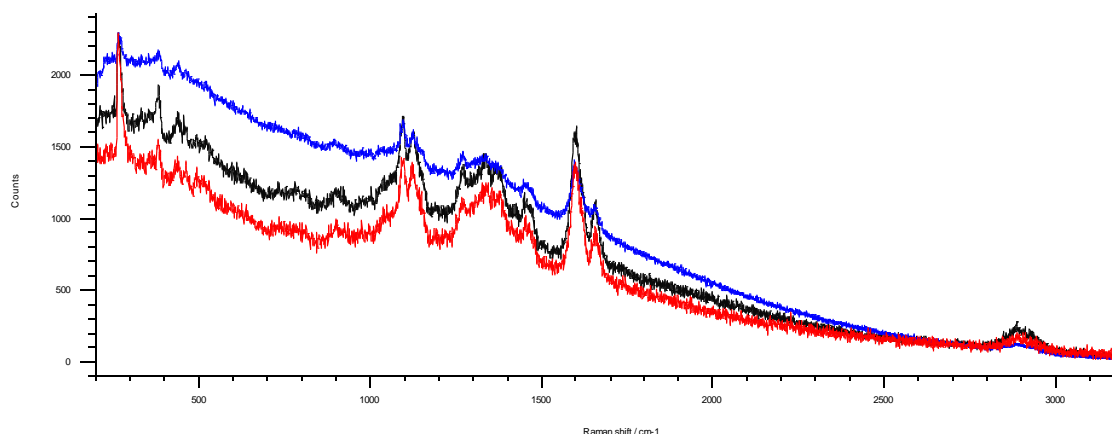
## 7.2 Materials and Methods

The evaluation of the effects of pelletising on wood materials was confined to “softspån” in this study. Softspån pellets as well as raw softspån shavings were supplied for the experimental work. The samples were stored in plastic bags under normal ambient laboratory conditions. For both Raman and XPS studies, individual pellets were split widthwise so that it was possible to analyse the shavings as well as the outer and inner surfaces of the pellets. In the case of XPS, handling was carried out with gloves in order to avoid sample contamination. This is especially important with XPS as oils and grease from finger contact or other sources can introduce false carbon/oxygen (C/O) readings.

Raman spectroscopy was carried out using a Renishaw Ramascope instrument with recently upgraded software and instrument controls. Spectra were run using a near-IR diode laser (785 nm) XPS analyses were undertaken using an automated Specs Sage 100 designed for high sample throughput with non-monochromated Al K $\alpha$  x-rays and a large spot (4 x 8 mm<sup>2</sup>) size.

## 7.3 Results

The result of running Raman spectroscopy on the three sample types (pellet outside, pellet inside and shavings) is shown in Figure 20 below.



**Figure 20 Raman spectra of softspån pellet outside (blue), shavings (black) and pellet inside (red).**

The baseline has not been subtracted from the spectra shown above; however, it is clear from these spectra and from other replications of this experiment that Raman spectroscopy did not show any differences between the three material types.

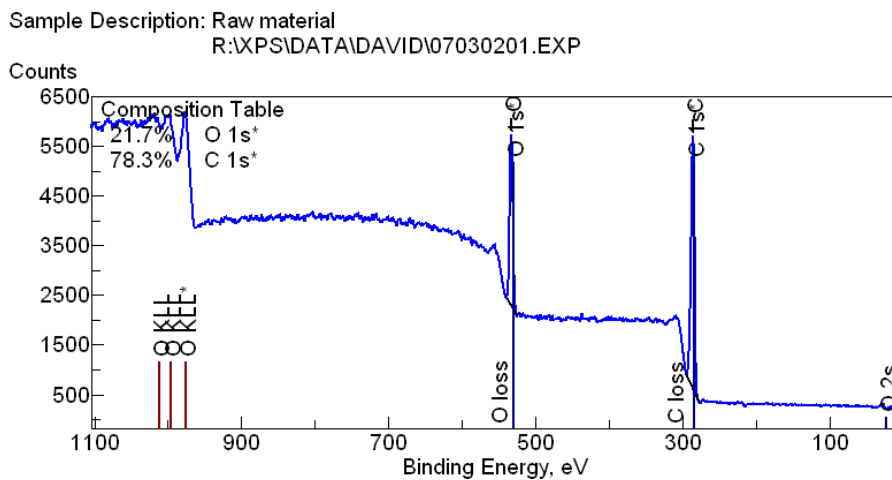
The results of XPS experiments (three per material type) are summarised in Table 1 in terms of mean carbon and oxygen atom% values and the resulting O/C ratio. Given the standard deviation expected for XPS analyses, the three wood sample types cannot be distinguished in terms of their surface chemistry based on this study. Examples of survey spectra for the three sample types are shown in Figure 21 to Figure 23. Figure 24 shows, as an example, the high resolution XPS spectrum for softspån shavings, in which the peak envelope has been deconvoluted to reveal a series of individual peaks reflecting the different carbon environments in the raw wood material. This is



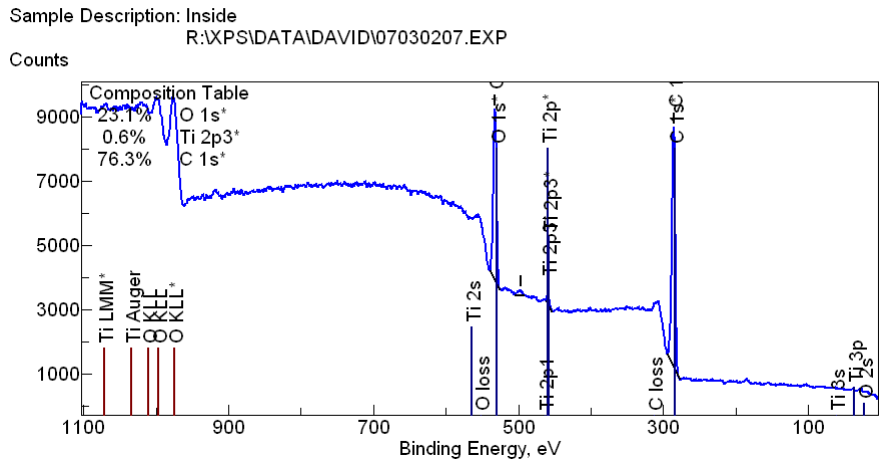
comparable to the high resolution spectrum for unextracted cherry wood obtained by Nzokou and Kamdem (41) (Figure 25) in terms of number of peaks and their binding energies; however, our XPS spectra are not as well resolved as those in their publication.

Material	O%	C%	O/C
Softspån shavings	21.5	78.5	0.27
Pellet inside	22.2	76.8	0.29
Pellet outside	23.4	75.9	0.31

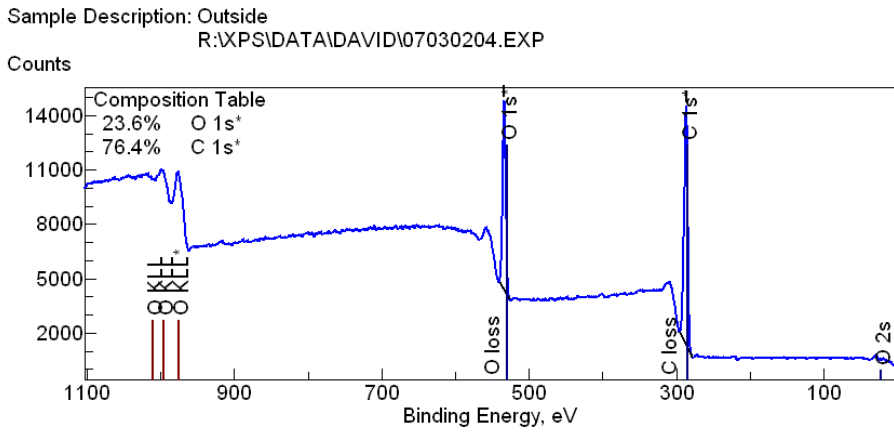
**Table 1: Mean values for XPS analyses of three softspån sample types.**



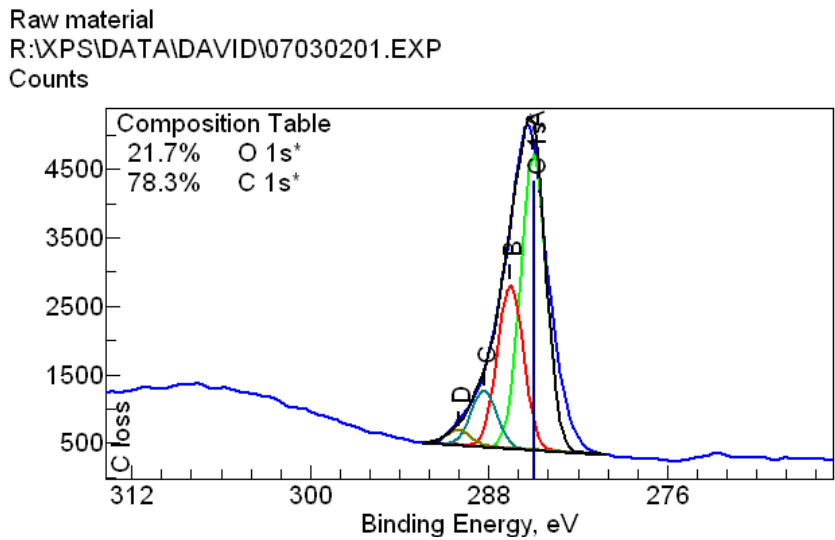
**Figure 21: XPS survey spectrum for Softspån shavings.**



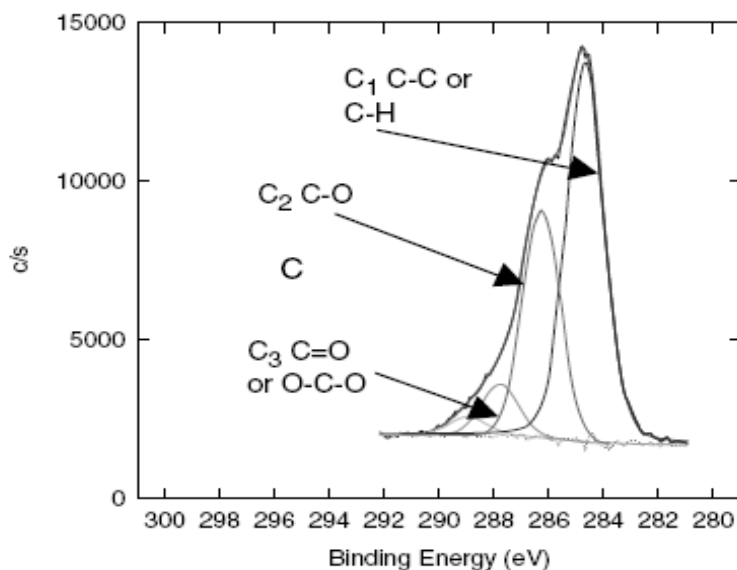
**Figure 22: XPS survey spectrum of softspån pellet inner surface.**



**Figure 23: XPS survey spectrum of softspån pellet outer surface.**



**Figure 24: High resolution XPS spectrum of softspån shavings.**



**Figure 25: High resolution XPS spectrum of unextracted cherry wood showing deconvoluted peaks for various carbon environments (from (41)).**

As a check on whether the time of exposure to X-rays could influence the XPS results, a much shorter exposure time was used in subsequent experiments; however, the results in terms of O/C ratio were much the same.

Interestingly, the results summarized in Table 1 show O/C ratios that are lower than expected based on the known components in wood. For example, the O/C ratios expected for lignin, cellulose and hemicelluloses are 0.34, 0.8 and 0.8 respectively. The low O/C ratios shown in Table 1 suggest a number of possibilities, either individually or in combination, namely, 1) a lignin-covered surface, 2) a preponderance of waxes on the wood surfaces, 3) contamination. Although a definitive answer is not possible, contributions from contaminants and waxes seem more likely as an explanation than the chance that all the sites analysed would consist predominantly of lignin. In any event, XPS analysis has also failed to distinguish between the three types of softspån material that were examined.

#### 7.4 Conclusions

Neither Raman spectroscopy nor XPS showed any chemical differences in the bulk or surface of softspån material as a result of the pelletising process and therefore it is clearly not possible at this stage to suggest that chemical changes in this material could contribute to differences in the quality characteristics of fuel pellets. A more extensive investigation including, for example, longer Raman spectra collection times and more closely controlled incoming raw material quality for XPS in combination with other pellet materials, might provide a more definitive study than was possible in this investigation.

## 8 Standards and standardization criteria.

### 8.1 European standardization for biomass

The development of European Standards (EN) is seen as a major driver to expand the market for solid biofuels. This market expansion is needed to fulfil the aims defined within the European Commission's White Paper on renewable energy, the directive on "green" electricity from renewable energy (EU-Directive COM(2000) 279 final), and the European Biofuel Directive as well as various political goals on the national level. Therefore the European Commission (EC) has given already a couple of years ago a mandate to CEN, the European Standardisation Organisation, to develop standards for solid biofuels. On that background a Technical Committee (TC) has been founded by CEN to develop such standards. For that purpose CEN TC 335 "Solid Biofuels" has established 5 Working Groups (WG's). The task of these WG's is it to develop based on the honorary work of experts proposals for Technical Specifications (TS's) to be transferred at a later stage to European Standards (EN's). The different WG's are summarised under the following topics:

- WG 1: Terminology, definition and description
- WG 2: Fuel specification and classes and quality assurance
- WG 3: Sampling and sample reduction
- WG 4: Physical-mechanical tests
- WG 5: Chemical tests

According to the different topics defined within the work plan of the CEN TC 335 proposals for Technical Specifications for solid biofuels have been developed by these WG's based on the best available knowledge within the last years. These proposals have been adapted or are on the way to be adapted by the different members of CEN TC 335 as Technical Specifications; these TS's are a kind of a pre-standard. The Technical Committee is currently preparing 30 technical specifications. In Table 2 a number of important technical specifications are mentioned.

Number CEN/TS	Title
14588	Terminology, definitions, descriptions
14774	Moisture determination
14775	Ash content
14778	Methods for sampling
14918	Calorific value
14961	Fuel specifications and classes
15103	Bulk density
15104	Determination of C, H and N
15148	Determination of volatiles
15149	Particle size distribution
15150	Particle density
15210	Durability of pellets.
15234	Quality assurance

**Table 2: 13 important technical specifications.**

The European standardisation work has been supported by so-called pre-normative research realised within the EC and national funded BioNorm project ("Pre-normative work on sampling and testing of solid biofuels for the development of quality assurance systems"). Within this project, which was running between 2002 and 2004, R&D work has been carried out in the field of sampling and sample reduction, physical-mechanical and chemical tests as well as quality assurance. This work has been very closely linked with the ongoing standardisation process. Without this valuable support directly integrated into the development of the TS's it would not have been possible to develop the TS's already available in the recognised high quality.

This European standardisation work is continued in the BioNorm II project ("Pre-normative research on solid biofuels for improved European standards") for the period 2007-2009. This project will focus on such aspects urgently needed by industry to increase the markets for solid biofuels where significant pre-normative R&D need is given. This applies in particular to an acceptable and transparent definition of the key properties of solid biofuels traded on the market, accounting for the given needs from the production and provision chain as well as the end user. Furthermore, reference test methods and rapid test methods are necessary to prove if the defined key properties are met. Additionally, rules for sampling and sample planning as well as quality measures especially adapted to the needs of solid biofuels are urgently needed. To achieve these goals, the existing Technical Specification on "Fuel specification and classes" developed by WG2 of CEN TC 335 will be improved in close collaboration with WG2 during the revision towards a full EN by adding:

- specifications given by the combustion unit, and
- rules for conformity of the products with their specified requirements.

To provide this information, the following aspects need to be addressed in detail:

- further improvement of existing reference tests in particular in terms of precision,
- development of new reference test methods,
- development of rapid on-site test methods,
- development of sampling and sample reduction methods for further materials and development of sampling plans,
- development of quality measures in accordance with the ISO 9000 family especially adapted to solid biofuels.

In chapters 8.2 and 8.3 CEN/TS 14961 Fuel specifications and classes and CEN/TS 15234 Quality assurance are more detailed described. The chapters illustrate how pellets and pellets production are described in the Technical Specifications. Chapter 8.4 is an extract from BioNorm where rawmaterials and quality criteriae for pellets are discussed.

## **8.2 CEN/TS 14961. Fuel specifications and classes**

The classification is based on the biofuel origin and source. In the hierarchical classification system the main origin-based solid biofuel groups are:

- woody biomass;
- herbaceous biomass;

- fruit biomass
- blends and mixtures.

*Woody biomass* is biomass from trees, bushes and shrubs.

*Herbaceous biomass* is from plants that have a non-woody stem and which die back at the end of the growing season.

*Fruit biomass* is the biomass from the parts of a plant which hold seeds.

The term “*Blends and mixtures*” refers to material of various origins within the given box in the classification table and appears on four levels. Blends are intentionally mixed biofuels, whereas mixtures are unintentionally mixed biofuels. The origin of the mixture or blend has to be described using Table 3, Table 4 and Table 5. If solid biofuel blend or mixture may contain chemically treated material it has to be stated. A blend or a mixture of e.g. chemically treated wood and chemically untreated wood has to be classified as chemically treated wood.

The second level of classification in Table 3, Table 4 and Table 5 describes fuels from different sources within the main groups, primarily stating whether the biomass is a by-product or a residue from the industry or if it is virgin material. Groups in Table 3, Table 4 and Table 5 are further divided into third and fourth level sub-groups.

The purpose of Table 3, Table 4 and Table 5 is to allow the possibility to differentiate and specify biofuel material based on origin with as much detail as needed. In Table 6 specifications of properties of wood pellets are shown.

Table 6 lists the normative properties, which have to be specified and informative properties, which are voluntary. Normative properties vary depending on both origin and traded form. With the help of typical values from Table 7 information on physical and chemical properties can be deducted.

Example: Wood pellets

#### **A.2 Wood pellets** (selected from Table 5)

Origin:	1.2.1.1 Chemically untreated wood, wood excluding bark
Moisture content:	M10
Mech durability:	DU97.5
Amount of fines:	F1.0 or F2.0
Dimensions:	D06 or D08
Ash content:	A0.7
Sulphur content:	S0.05
Additives:	< 2 w-% of dry basis. Only products from the primarily agricultural and forest biomass that are not chemically modified are approved to be added as a pressing aids. Type and amount of additive has to be stated.
Net calor value	E4.7 ( $E_{ar} \geq 4,7 \text{ kWh/kg} = 16,9 \text{ MJ/kg}$ )

1. Woody biomass	1.1 Forest and plantation wood	1.1.1 Whole trees	1.1.1.1 Deciduous wood
			1.1.1.2 Coniferous wood
			1.1.1.3 Short rotation coppice
			1.1.1.4 Bushes
			1.1.1.5 Blends and mixtures
		1.1.2 Stemwood	1.1.2.1 Deciduous
			1.1.2.2 Coniferous
			1.1.2.3 Blends and mixtures
		1.1.3 Logging residues	1.1.3.1 Fresh/Green (including leaves/needles)
			1.1.3.2 Dry
			1.1.3.3 Blends and mixtures
		1.1.4 Stumps	1.1.4.1 Deciduous wood
			1.1.4.2 Coniferous wood
	1.1.4.3 Short rotation coppice		
	1.1.4.4 Bushes		
	1.1.4.5 Blends and mixtures		
	1.1.5 (from forestry operations)* Bark		
	1.1.6 Landscape management woody biomass		
	1.2 Wood processing industry, by-products and residues	1.2.1 Chemically untreated wood residues	1.2.1.1 Wood without bark
			1.2.1.2 Wood with bark *
			1.2.1.3 (from industry Barkoperations)*
			1.2.1.4 Blends and mixtures
		1.2.2 Chemically treated wood residues	1.2.2.1 Wood without bark
			1.2.2.2 Wood with bark *
			1.2.2.3 (from industry Barkoperations) *
			1.2.2.4 Blends and mixtures
1.2.3 Fibrous waste from pulp and paper industry		1.2.3.1 Chemically untreated fibrous waste	
		1.2.3.2 Chemically treated fibrous waste	
1.3 Used wood		1.3.1 Chemically untreated wood	1.3.1.1 Wood without bark
			1.3.1.2 Bark*
	1.3.1.3 Blends and mixtures		
	1.3.2 Chemically treated wood	1.3.2.1 Wood without bark	
		1.3.2.2 Bark*	
		1.3.2.3 Blends and mixtures	
1.4 Blends and mixtures			

**Table 3: Classification of origin and sources of woody biomass**

2 Herbaceous biomass	2.1 Agriculture and Horticulture herb	2.1.1 Cereal crops	2.1.1.1 Whole plant
			2.1.1.2 Straw parts
			2.1.1.3 Grains or seeds
			2.1.1.4 Husks or shells
			2.1.1.5 Blends and mixtures
		2.1.2 Grasses	2.1.2.1 Whole plant
			2.1.2.2 Straw parts
			2.1.2.3 Seeds
			2.1.2.4 Shells
			2.1.2.5 Blends and mixtures
		2.1.3 seed crops Oil	2.1.3.1 Whole plant
			2.1.3.2 Stalks leaves and
			2.1.3.3 Seeds
			2.1.3.4 Husks or shells
			2.1.3.5 Blends and mixtures
		2.1.4 Root crops	2.1.4.1 Whole plant
			2.1.4.2 Stalks leaves and
	2.1.4.3 Root		
	2.1.4.4 Blends and mixtures		
	2.1.5 Legume crops	2.1.5.1 Whole plant	
		2.1.5.2 Stalksand leaves	
		2.1.5.3 Fruit	
		2.1.5.4 Pods	
		2.1.5.5 Blends and mixtures	
	2.1.6 Flowers	2.1.6.1 Whole plant	
		2.1.6.2 Stalksand leaves	
		2.1.6.3 Seeds	
		2.1.6.4 Blends and mixtures	
	2.1.7 Landscape management herbaceous biomass		
	2.2 Herb processing industry, by-products and residues	2.2.1 Chemically untreated herb residues	2.2.1.1 Cereal crops and grasses
2.2.1.2 Oil seed crops			
2.2.1.3 Root crops			
2.2.1.4 Legume crops and flowers			
2.2.1.5 Blends and mixtures			
2.2.2 Chemically treated herb residues		2.2.2.1 Cereal crops and grasses	
		2.2.2.2 Oil seed crops	
		2.2.2.3 Root crops	
		2.2.2.4 Legume crops and flowers	
		2.2.2.5 Blends and mixtures	
2.3 Blends and mixtures			

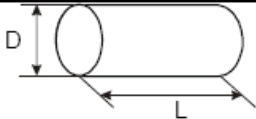
**Table 4: Classification of origin and sources of herbaceous biomass**



3 Fruit biomass	3.1 Orchard and horticulture fruit	3.1.1 Berries	3.1.1.1 Whole berries
			3.1.1.2 Flesh
			3.1.1.3 Seeds
			3.1.1.4 Blends and mixtures
		3.1.2 Stone/kernel fruits	3.1.2.1 Whole fruit
			3.1.2.2 Flesh
			3.1.2.3 Stone/kernel
			3.1.2.4 Blends and mixtures
		3.1.3 Nuts and acorns	3.1.3.1 Whole nuts
			3.1.3.2 Shells/husks
			3.1.3.3 Kernels
			3.1.3.4 Blends and mixtures
	3.2 Fruit processing industry, by-products and residues	3.2.1 Chemically untreated fruit residues	3.2.1.1 Berries
			3.2.1.2 fruits
			Stone/kernel
3.2.1.3 Nuts and acorns			
3.2.1.4 Crude olive cake			
3.2.1.5 Blends and mixtures			
3.2.2 Chemically treated fruit residue		3.2.2.1 Berries	
		3.2.2.2 fruits	
		Stone/kernel	
		3.2.2.3 Nuts and acorns	
	3.2.2.4 Exhausted olive cake		
3.2.2.5 Blends and mixtures			
3.3 Blends and mixtures			
4 Blends and mixtures	4.1 Blends		

**Table 5: Classification of origin and sources of fruit biomass**

**Table 6 Specification for properties of pellets**

<b>Master table</b>			
<b>Origin:</b> According to 6.1 and Table 1		Woody biomass (1), Herbaceous biomass (2), Fruit biomass (3), Blends and mixtures (4)	
<b>Traded Form</b> (see Table 2)		Pellets	
<b>Normative</b>	<b>Dimensions (mm)</b>		
			
	<b>Diameter (D) and Length (L)<sup>a</sup></b>		
	D06	≤ 6 mm ± 0,5 mm and L ≤ 5 x Diameter	
	D08	≤ 8 mm ± 0,5 mm, and L ≤ 4 x Diameter	
	D10	≤ 10 mm ± 0,5 mm, and L ≤ 4 x Diameter	
	D12	≤ 12 mm ± 1,0 mm, and L ≤ 4 x Diameter	
	D25	≤ 25 mm ± 1,0 mm, and L ≤ 4 x Diameter	
	<b>Moisture (w-% as received)</b>		
	M10	≤ 10 %	
	M15	≤ 15 %	
	M20	≤ 20 %	
	<b>Ash(w-% of dry basis)</b>		
	A0.7	≤ 0,7%	
	A1.5	≤ 1,5 %	
	A3.0	≤ 3,0 %	
	A6.0	≤ 6,0 %	
A6.0+	> 6,0 % (actual value to be stated)		
<b>Sulphur (w-% of dry basis)</b>			
S0.05	≤ 0,05 %	Sulphur is normative only for chemically treated biomass and if sulphur containing additives have been used	
S0.08	≤ 0,08 %		
S0.10	≤ 0,10 %		
S0.20+	> 0,20 % (actual value to be stated)		
<b>Mechanical durability (w-% of pellets after testing )</b>			
DU97.5	≥ 97,5 %		
DU95.0	≥ 95,0 %		
DU90.0	≥ 90,0 %		
<b>Amount of fines (w-%, &lt; 3,15 mm) after production at factory gate<sup>a</sup></b>		<sup>a</sup> At the last possible place in the production site	
F1.0	≤ 1,0 %		
F2.0	≤ 2,0 %		
F2.0+	> 2,0 % (actual value to be stated)		
<b>Additives (w-% of pressing mass)</b>			
Type and content of pressing aids, slagging inhibitors or any other additives have to be stated			
<b>Nitrogen, N (w-% of dry basis)</b>		Nitrogen is normative only for chemically treated biomass	
N0.3	≤ 0,3 %		
N0.5	≤ 0,5 %		
N1.0	≤ 1,0 %		
N3.0	≤ 3,0 %		
N3.0+	> 3,0 % (actual value to be stated)		
<b>Informative</b>	Net calorific value, $q_{p,net,gr}$ (MJ/kg as received) or energy density, $E_{gr}$ (kWh/ m <sup>3</sup> loose)		Recommended to be informed by retailer.
	<b>Bulk density as received (kg/m<sup>3</sup> loose)</b>		Recommended to be stated if traded by volume basis
	Chlorine, Cl (weight of dry basis, w-%)		Recommended to be stated as a category Cl 0.03, Cl 0.07, Cl 0.10 and Cl 0.10+ (if Cl > 0,10 % the actual value to be stated)
<sup>a</sup> Maximum 20 % of the pellets may have a length of 7,5 x Diameter.			

Parameter	Unit	Coniferous wood (1.1.2.2 and 1.2.1.1)		Deciduous wood (1.1.2.1 and 1.2.1.1)	
		Typical value	Typical variation	Typical value	Typical variation
Ash	% w/w d	0,3	0,2 to 0,5	0,3	0,2 to 0,5
Gross calorific value $q_{gr,daf}$	MJ/kg daf	20,5	20,2 to 20,8	20,2	19,5 to 20,4
Net calorific value $q_{n,daf}$	MJ/kg daf	19,2	18,8 to 19,8	19,0	18,5 to 19,2
Carbon, C	w-% daf	51	47 to 54	49	48 to 52
Hydrogen, H	w-% daf	6,3	5,6 to 7,0	6,2	5,9 to 6,5
Oxygen, O	w-% daf	42	40 to 44	44	41 to 45
Nitrogen, N	w-% daf	0,1	< 0,1 to 0,5	0,1	<0,1 to 0,5
Sulphur, S	w-% daf	0,02	< 0,01 to 0,05	0,02	< 0,01 to 0,05
Chlorine, Cl	w-% daf	0,01	< 0,01 to 0,03	0,01	< 0,01 to 0,03
Fluorine, F	w-% daf	< 0,000 5	< 0,000 5	< 0,000 5	< 0,000 5
Al	mg/kg d	100	30 to 400	20	< 10 to 50
Ca	mg/kg d	900	500 to 1 000	1 200	800 to 20 000
Fe	mg/kg d	25	10 to 100	25	10 to 100
K	mg/kg d	400	200 to 500	800	500 to 1 500
Mg	mg/kg d	150	100 to 200	200	100 to 400
Mn	mg/kg d	147		83	
Na	mg/kg d	20	10 to 50	50	10 to 200
P	mg/kg d	60	50 to 100	100	50 to 200
Si	mg/kg d	150	100 to 200	150	100 to 200
Ti	mg/kg d	< 20	<20	<20	<20
As	mg/kg d	< 0,1	< 0,1 to 1,0	< 0,1	< 0,1 to 1,0
Cd	mg/kg d	0,10	< 0,05 to 0,50	0,10	< 0,05 to 0,50
Cr	mg/kg d	1,0	0,2 to 10,0	1,0	0,2 to 10,0
Cu	mg/kg d	2,0	0,5 to 10,0	2,0	0,5 to 10,0
Hg	mg/kg d	0,02	< 0,02 to 0,05	0,02	< 0,02 to 0,05
Ni	mg/kg d	0,5	< 0,1 to 10,0	0,5	< 0,1 to 10,0
Pb	mg/kg d	2,0	< 0,5 to 10,0	2,0	< 0,5 to 10,0
V	mg/kg d	< 2	< 2	< 2	< 2
Zn	mg/kg d	10	5 to 100	10	5 to 100

a Data is obtained from a combination of mainly Swedish, Finnish, Danish, Dutch and German research. The values only aim to describe properties that can be expected in Europe in general.

**Table 7**  
**: Typical values for virgin wood materials, with or without insignificant amounts of bark, leaves and needles .**

There are similar tables for bark, hay, straw, logging residues and short rotation coppice.

### 8.3 CEN/TS 15234. Quality Assurance

The objective of the Technical Specification is to serve as a tool to enable the efficient trading of biofuels. This means:

- the end-user can find a fuel that corresponds to his needs;
- the producer/supplier can produce a fuel with defined and consistent properties and describe the fuel to the customers.

Quality assurance measures should establish confidence in the product through systems that are simple to operate and do not cause undue bureaucracy. Solid biofuels are specified according to CEN/TS 14961—Solid Biofuels, Fuel Specification and Classes. With a proper quality assurance procedure and specification of origin and source (i.e. kind of biofuel) in the whole production chain, it is possible to reduce or eliminate the parameters that need analysing. If the company does not have a quality management system, this Technical Specification can be used on its own to help the supplier in documenting fuel quality and creating adequate confidence between the supplier and the end-user.

The Technical Specification covers the Fuel Quality Assurance of the supply chain and the information to be used in the quality control of the product. This ensures traceability and gives confidence by demonstrating that all processes along the supply chain (of solid biofuels) up to the point of the delivery to the end-user are under control. Procedures to establish confidence in the product include the following requirements:

- the first operator in the biofuel supply chain shall document the origin and source of the biofuel.
- the biofuel shall be traceable through the entire supply chain
- the biofuel producer shall take quality assurance measures to achieve and secure product quality
- transportation, handling and storage of the product should be performed with care and shall be documented by the operator
- the supplier to the end-user or retailer is responsible for the biofuel quality and shall make a Fuel Quality Declaration
- for specifications in the Fuel Quality Declaration CEN/TS 14961 shall be used.
- The Fuel Quality Declaration shall include:
  1. origin and source
  2. country where the biomass is harvested or first traded as biofuel
  3. traded form
  4. properties

Figure 26 is an example of documentation in 6 steps on a wood pellet production factory. The production chain described is for big sacks used in private households.

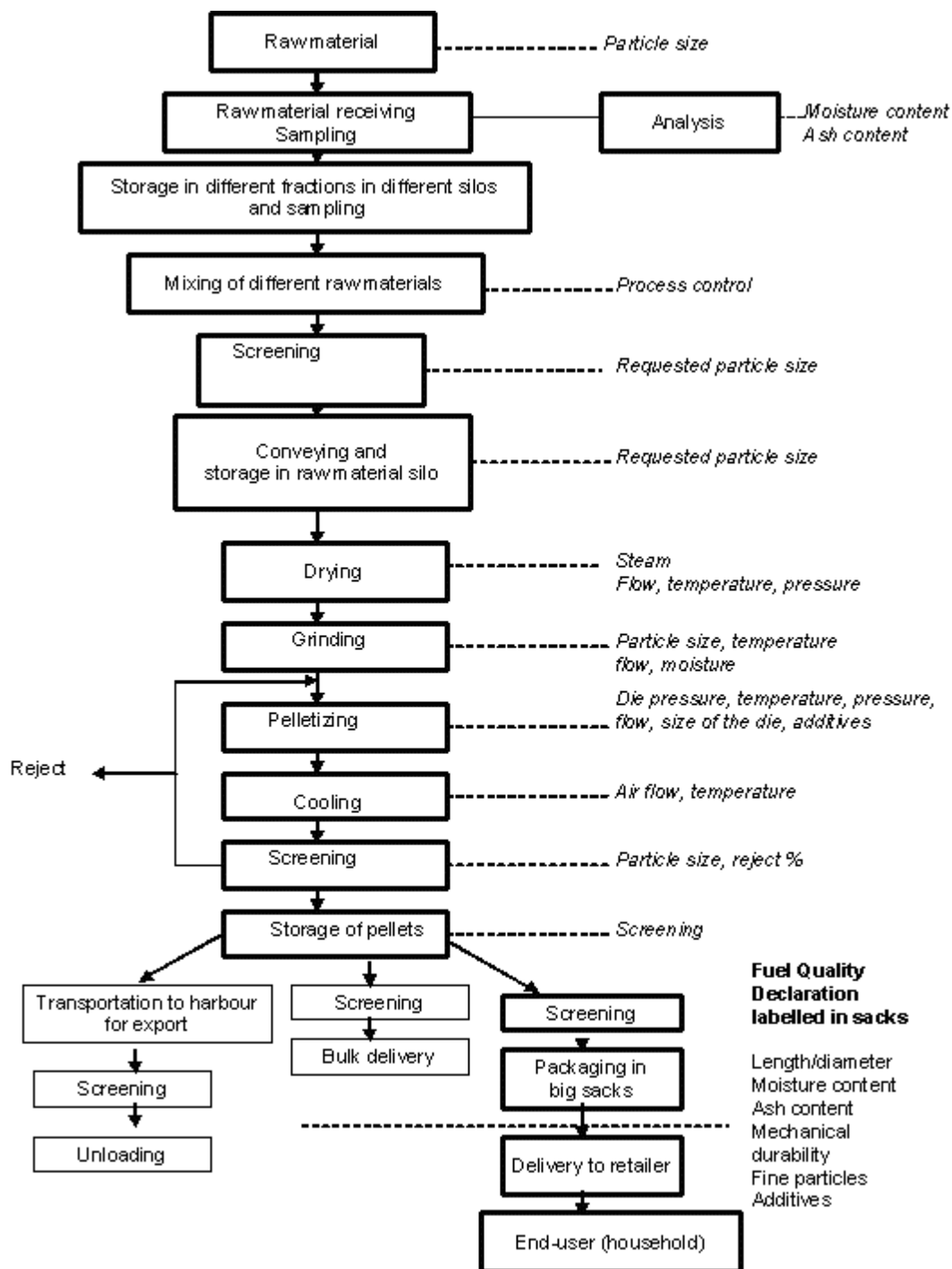


Figure 26. Wood pellet production chain.

### **Step 1. Production description (documentation of steps in the production chain)**

This is an example of pellet production for a large company, annual production is about 100 000 tons. Wood pellet production includes several production phases. Figure 26 describes the different phases and also the Critical Control Points (marked by *italic*, which are only for internal use) that affect the quality of the fuel.

### **Step 2. Product specification (packaged pellets)**

- CEN/TS 14961:2005: Normative: 1.2.1.1 Wood without bark, wood pellets D06, M10, DU97.5, F1.0, <2 w-% starch used as additive
- Quality information is labelled on packages (big sacks)

### **Step 3. Quality influencing factors including company performance**

- Raw material
- Storage of raw material
- Equipment
- Pelletizing process
- Proficiency of staff

### **Step 4. Critical Control Points for compliance with the product specification**

- Selection of the raw material (origin and source)
- Reception/storage/sampling of raw material (condition of the store, no impurities, sampling methods)
- Blending of different raw materials (process control)
- Transportation (suitable conveying equipment)
- Screenings (requested particle size)
- Drying (air flow, temperature control)
- Grinding (homogenous raw material)
- Pelletizing (pre-treatment/additives, equipment)
- Storage of the pellets (different quality classes, condition of the store, no impurities)
- Packing of the pellets (avoid crushing of pellets).
- Delivering pellets to the retailer and/or end user (no impurities, fulfil approved quality specifications)

### **Step 5. Measures to give confidence to customers that the specification(s) are being realised**

- Visual inspection during the whole process chain (colour, check for odour, size, durability of pellets)
- Moisture content before pelletizing and when delivery to the end-user (analysis and work instructions)
- Determination of properties after production (amount of fines, dimensions, moisture content, mechanical durability, ash content)
- Production control, conditions and adjustment of the equipment
- Measurement of certain properties after raw material basis is changed on a frequency appropriate to the process requirements
- Equipment is repaired or changed when necessary; some parts will require changing regularly according to the nature of the production control system

### **Step 6. Routines for separate handling of nonconforming materials and products**

If wood pellets are not fulfilling the requirements, these batches have to be stored separately from conformed product. All necessary information has to be filed. If nonconformity is discovered at the premises of the consumer in connection with delivery, a nonconformity report is generated and handling of the nonconforming lot is agreed with the consumer.

#### 8.4 Example from BioNorm: Selection of raw materials and durability of pellets.

In the BioNorm project (2002-2004) 15 different types of biofuel pellets based on different raw materials (Figure 27 and Table 8) were tested. The pellets are produced of softwood, hardwood, mixed wood and agro residues. The CEN/TS 14961 specifications for the materials are listed in Table 8.



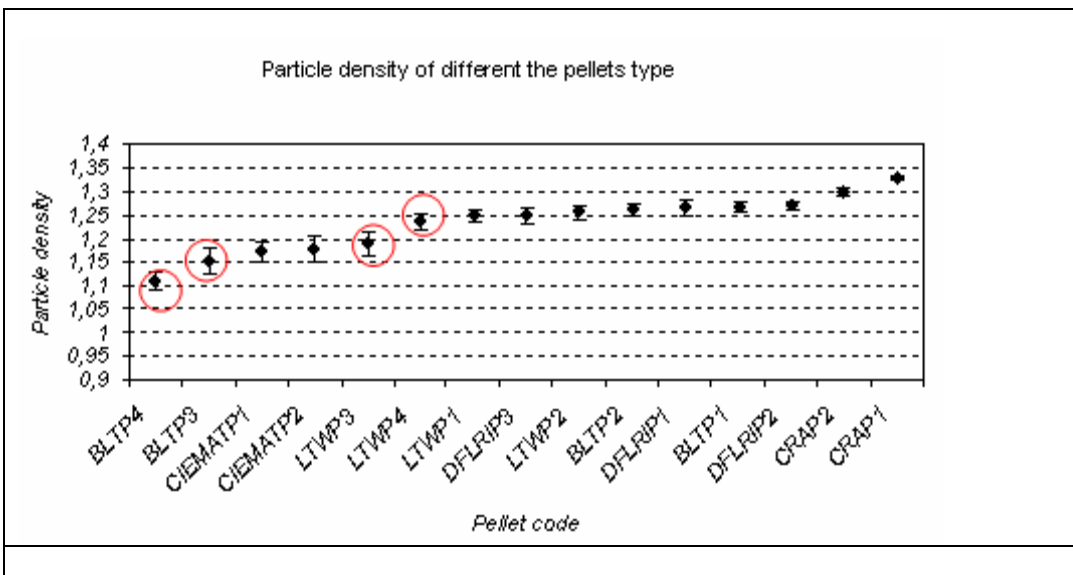
Figure 27. Samples of the 15 different pellets tested in the BioNorm project

Tabel 8. Description of the pellets and classification according to CEN/TC 14961 Fuel specifications and classes

Sample name	Diameter (mm)	Raw material	CEN/TC 14961 Classification
CRAP P1	6	Mixed wood	1.1.2.3
CRAP P2	6	Softwood	1.1.2.2
Ciemat P1	6	Hardwood	1.1.2.1
Ciemat P2	6	Hardwood	1.1.2.1
DFLRI P1	8	Mixed wood	1.1.2.3
DFLRI P2	8	Mixed wood	1.1.2.3
DFLRI P3	8	Mixed wood	1.1.2.3
LTW P1	6	Mixed wood	1.1.2.3
LTW P2	6	Mixed wood	1.1.2.3
LTW P3	9	Straw	2.1.1.2
LTW P4	6	Mischanthus	2.1.2.1
BLT P1	6	Softwood	1.1.2.2
BLT P2	6	Softwood	1.1.2.2
BLT P3	8	Hay	2.1.2.2
BLT P4	9	Straw	2.1.1.2

**Table 8 Description of the pellets and classification according to CEN/TC 14961 Fuel specifications and classes.**

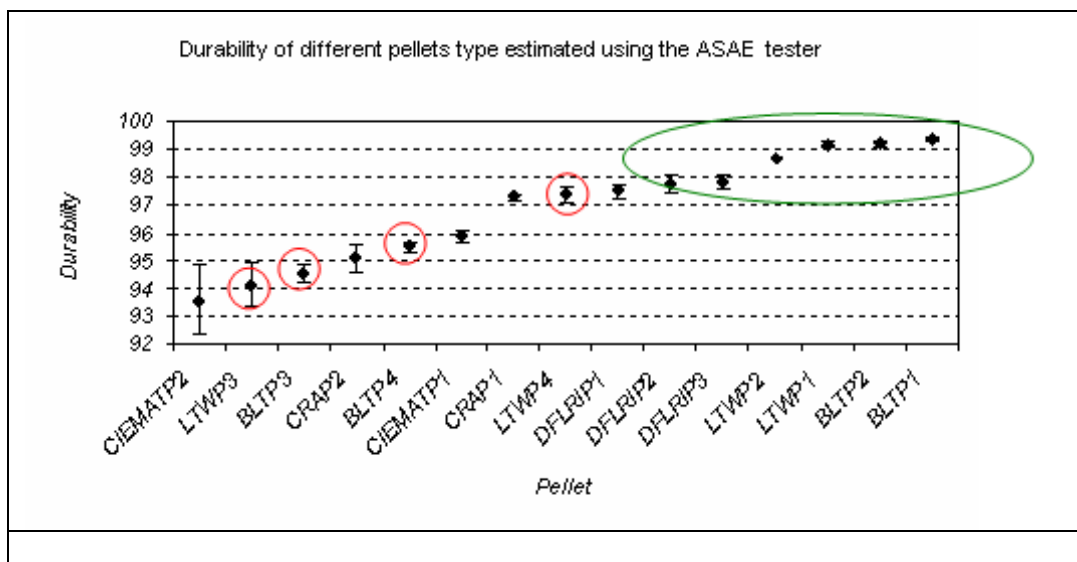
The particle density is tested according to CEN/TC 15150 and varies for the 15 pellets between 1,1 – 1,35 g cm<sup>-2</sup>. The pellets produced of straw, hay and miscanthus do all have a low particle density. This indicates that the raw material quality has an influence on the pellet quality. But also the two hardwood pellets have a low density indication an influence from the pelletizing process. See Figure 28.



**Figure 28 Particle density of the 15 different pellets. The red marked are pellets made of agro residues**



The mechanical durability of the 15 pellets is tested according to CEN/TC 15210-1 and varies between 93,5 and 99,5 % (Figure 29). The limit value for high quality pellets according to CEN/TC 15210-1 is 97,5 %. The test indicates that there is a major variety in the mechanical durability in the 15 samples, and this is not unambiguously connected to the quality of the raw material. The main reason for the lower quality of the wood pellets is probably that they are produced in Spain and Belgium where the experience in pellet production is low.



**Figure 29. Mechanical durability of the 15 pellets. The red marked are pellets made of agro residues. The green marked are pellets with a mechanical durability over 97,5%.**

## 9 General conclusions

This project has been initiated in order to establish a fundamental understanding of the pelletization process. The major results of the project are published in the papers listed in the beginning of the report (See abstracts in chapter 3).

Reference (6) presents a theoretical model that describes the development of mechanical forces within the press channel. It is shown that the pelletizing forces increase exponentially as a function of the press channel length. The magnitude of the pelletizing force is furthermore influenced by the friction coefficient between the pellet and the press channel, the diameter of the press channel and the specific biomass species in question.

Reference (5) presents an experimental verification of the pellet model. In this paper it is shown that the pelletizing pressure does indeed increase exponentially as predicted in the model. Secondly, it is shown that the pressure curve increases more rapidly for beech as compared to pine, in agreement with the experience from large scale pellet production. Finally, the procedure for using a single pelleter unit as a means for simulating an industrial pelletizing process in a controllable way is described.

The light- and electron microscopy studies show that the structure of wood is complex and hierarchical, thus allowing for the specific mechanical properties giving wood its unique characteristics as a construction material. The presence of long tubular cells is important in

modelling the behaviour of wood raw material in a channel press. A surprising degree of organized structure is preserved in the pressed pellets thus giving the pellet an overall density lower than the density of the cell wall material.

Neither Raman spectroscopy nor XPS showed any chemical differences in the bulk or surface of “softspån” material as a result of the pelletizing process and therefore it is clearly not possible at this stage to suggest that chemical changes in this material could contribute to differences in the quality characteristics of fuel pellets. A more extensive investigation including, for example, longer Raman spectra collection times and more closely controlled incoming raw material quality for XPS in combination with other pellet materials, might provide a more definitive study than was possible in this investigation.

The research performed in this project is at a very early stage compared to the process of standardisation (chapter 8). The methods described in CEN with Technical Reports (TR), Technical Specifications (TS), Guidelines (pre-standards) and Standards are tested and discussed in projects and Working Groups over years in different institutions, universities and companies.

The findings related to the structural and chemical characterization of pellets and standardization are still on a preliminary level. The results concerning the development of mechanical forces in the press channels represent new knowledge to the research field of biomass pelletization. However, the link between the mechanical forces and the chemical adhesion forces has not been explored in detail yet. This issue will be investigated in the second phase of the project. The general ambition in the second phase of the project must be to make the first version of a Technical Report which can be discussed in our Danish and European network for pellet researchers and end-users.

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