Pasi Karinkanta

DRY FINE GRINDING OF NORWAY SPRUCE (PICEA ABIES) WOOD IN IMPACT-BASED FINE GRINDING MILLS
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**Abstract**

Wood powders are used in numerous applications such as thermoplastics and filters, and a lot of research effort has been put into developing novel ways of utilising them. The mechanical processing of wood powders, especially at particle sizes below 100 µm, has been reported in several studies, but they lack information on the effect of fine grinding conditions on the particle morphology and cellulose crystallinity, both of which are important parameters in the further processing of wood powders and in their various applications. This makes it very difficult to design and optimise fine grinding processes with different applications in mind. The aim of this thesis was to study the dry fine grinding of wood in several impact-based fine grinding mills in order to find out their effect on the properties of the wood and to study the energy required for the mechanical processing of the resulting powders.

The effect of the main operational parameters on the properties of dried Norway spruce wood and the energy consumption was studied using three impact-based fine grinding mills that were capable of pulverising the wood down to a median particle size of less than 25 µm. It was found that the impact events occurring in media mills can be used for the production of very fine wood powders with lower cellulose crystallinity and rounder shaped particles having more uniform shape distribution than powders pulverised to a similar size range by means of impact events in non-media mills. A practical estimate was obtained for the minimum specific energy consumption in fine grinding in mills involving grinding media that could be utilised as a target for optimisation. Impact-based media milling under cryogenic conditions can be used to obtain different Norway spruce wood powders from those produced under ambient grinding conditions, i.e. without the freezing effect of nitrogen liquid. The energy efficiency of fine grinding can be enhanced by choosing cryogenic rather than ambient conditions. The moisture content of the wood has greater influence on the size and shape of the particles when milling is accomplished under ambient conditions. Torrefaction can reduce the energy consumption in impact-based media mills for median particle sizes over 17.4 µm (± 0.2 µm), while the shape and cellulose crystallinity of the particles are not significantly affected by torrefaction pretreatment as a function of energy consumption.

**Keywords:** aspect ratio, cellulose crystallinity, comminution, dry fine grinding, energy consumption, Norway spruce, particle size, processing, wood flour, wood powder
Puujauheita käytetään laajalti erilaisissa sovelluksissa, kuten esimerkiksi biokomposiiteissa ja suodattimissa. Tämän lisäksi on olemassa paljon tutkimustietoa siitä, kuinka puujauheita voitaisiin hyödyntää laajemminkin. Puu voidaan mekaanisesti prosessoida alle 100 µm:n kokoluokkaan, mutta yksityiskohtaita tietoa kuivahienojauhauksen olosuhteiden vaikutuksesta jauheiden morfologiaan ja selluloosan kiteisyyteen ei ole saatavilla. Puuauheen morfologia ja selluloosan kiteisyydessä on kuitenkin merkittävää vaikutus sovelluksiin ja jatkojalostusta ajatellen. Puun kuivahienojauhauksen tiedon puute hankaloittaa merkittävästi prosessin suunnittelua ja optimointia erilaisia sovelluksia varten. Tämän väistökirjan tavoitteena on selvittää iskuihin perustuvien hienojauhimien vaikutukset puun ominaisuuksien ja tutkia mekaanisen prosessoinnin energiatehokkuutta hienojauhauksessa.

Tutkimuksessa selvitettiin kolmen erilaisten iskuihin perustuvan hienojauhauksmyllyn pääasiallisten operointiparametrien vaikutusta kuivatun metsäkuusen ominaisuuksiin ja energiankulutukseen. Jokaisella hienojauhaukseella onnistuttiin tuottamaan puujauhooja, joiden mediaanikoko oli alle 25 µm. Iskuihin perustuvalla jauhinkappalemyllyllä saatiin tuotettua puujauhoa, jonka selluloosan kiteisyys on alhaisempi ja partikkelimuodot pyöreämpiä verrattuna samankokoisiin puujauhoihin, jotka on tuotettu iskuihin perustuvalla jauhinkappaleetomilla hienojauhauksmyllyllä. Työssä saatiin käytännöllinen arvio kuivatun metsäkuusen hienojauhauksen minimienergiankulutuksesta iskuihin perustuville jauhinkappalemyllyille, mitä voidaan käyttää kyseisten myllytyypien optimoinnin tavoitteena. Työssä havaittiin lisäksi, että kryogeenisiä jauhauksosuhteita käyttämällä voidaan tuottaa erilaisia puujauhoja verrattuna puujauhoihin, jotka prosessoidaan ilman nestetyppijäädytystä, kun jauhatus suoritetaan iskuihin perustuvalla jauhinkappalemyllyllä. Ilman nestetyppijäädytystä puun kosteuteen kiistellään, mutta energeticellä voidaan parantaa myös jauhauksen energiatehokkuutta. Torrefinoinnilla voidaan vähentää hienojauhauksen energiankulutusta iskuihin perustuvilla jauhinkappalemyllyllä, kun tavoitteekoon mediaani on yli 17,4 µm (± 0,2 µm). Torrefinoinilla ei ole vaikutusta selluloosan kiteisyyteen tai partikkeleiden muotoon energiankulutuksen funktiona.

Asiasanat: aspektisuhde, energiankulutus, hienonmus, kuivahienojauhatus, metsäkuusi, partikkelikoko, prosessointi, puujauho, selluloosan kiteisyy
Dedicated to my beloved brother, Marko Karinkanta
Acknowledgements

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Oulu, 2014

Pasi Karinkanta
## List of abbreviations and symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_S$</td>
<td>Coefficients of classifier speed in the empirical models for air classifier milling</td>
</tr>
<tr>
<td>CML</td>
<td>Compound middle lamella of the wood cell wall</td>
</tr>
<tr>
<td>EW</td>
<td>Earlywood</td>
</tr>
<tr>
<td>FSP</td>
<td>Fibre saturation point</td>
</tr>
<tr>
<td>High GP</td>
<td>Jet milling experiments in which the average overpressure of the grinding air was approximately 10 bar</td>
</tr>
<tr>
<td>I(long)</td>
<td>Coefficients of the rotational direction of a rotor towards a long edge in the empirical models for air classifier milling</td>
</tr>
<tr>
<td>I(short)</td>
<td>Coefficients of the rotational direction of a rotor towards a short edge in the empirical models for air classifier milling</td>
</tr>
<tr>
<td>L</td>
<td>Direction towards the longitudinal axis of wood</td>
</tr>
<tr>
<td>Low GP</td>
<td>Jet milling experiments in which the average overpressure of the grinding air was approximately 6 bar</td>
</tr>
<tr>
<td>LW</td>
<td>Latewood</td>
</tr>
<tr>
<td>$M_S$</td>
<td>Coefficients of mill speed in the empirical models for air classifier milling</td>
</tr>
<tr>
<td>MC</td>
<td>Moisture content (%)</td>
</tr>
<tr>
<td>MFA</td>
<td>Microfibrillar angle</td>
</tr>
<tr>
<td>ML</td>
<td>Middle lamella of the wood cell wall</td>
</tr>
<tr>
<td>P</td>
<td>Primary layer of the wood cell wall</td>
</tr>
<tr>
<td>R</td>
<td>Direction towards the radial axis of wood</td>
</tr>
<tr>
<td>$S_1$, $S_2$, $S_3$</td>
<td>Secondary wall layers 1, 2 and 3 in the cell wall of tracheids</td>
</tr>
<tr>
<td>T</td>
<td>Direction towards the tangential axis of wood</td>
</tr>
<tr>
<td>WR</td>
<td>Wood ray</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>End-to-end amplitude of the oscillation movement in oscillatory ball milling (m)</td>
</tr>
<tr>
<td>$AR_{10}$</td>
<td>Aspect ratio corresponding to a value of 10% in the cumulative projected area-based aspect ratio distribution</td>
</tr>
<tr>
<td>$AR_{50}$</td>
<td>Median aspect ratio in the projected area-based aspect ratio distribution</td>
</tr>
<tr>
<td>$AR_{90}$</td>
<td>Aspect ratio corresponding to a value of 90% in the cumulative projected area-based aspect ratio distribution</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>CrI</td>
<td>Crystallinity index according to Segal et al. (1959) (%)</td>
</tr>
<tr>
<td>( d_{s,X} )</td>
<td>Sieve aperture with X% material pass (m)</td>
</tr>
<tr>
<td>( d_{10} )</td>
<td>Particle diameter corresponding to a value of 10% in the cumulative volume-based particle size distribution according to the laser diffraction method (µm)</td>
</tr>
<tr>
<td>( d_{50} )</td>
<td>Median particle size in the volume-based particle size distribution according to the laser diffraction method (µm)</td>
</tr>
<tr>
<td>( d_{90} )</td>
<td>Particle diameter corresponding to a value of 90% in the cumulative volume-based particle size distribution according to the laser diffraction method (µm)</td>
</tr>
<tr>
<td>( E_k )</td>
<td>Estimated kinetic energy of the grinding ball during one end-wall collision period (J)</td>
</tr>
<tr>
<td>( E_T )</td>
<td>Estimated total kinetic energy of the grinding ball during oscillatory ball milling, also referred to as the total available impact energy (J)</td>
</tr>
<tr>
<td>( f )</td>
<td>Oscillation frequency in oscillatory ball milling (Hz)</td>
</tr>
<tr>
<td>( M_{\text{air}} )</td>
<td>Molar mass of air (g mol(^{-1}))</td>
</tr>
<tr>
<td>( m )</td>
<td>Mass of the feed (g)</td>
</tr>
<tr>
<td>( m_{\text{ball}} )</td>
<td>Mass of the grinding ball (g)</td>
</tr>
<tr>
<td>( m_{\text{P,dry}} )</td>
<td>Dry mass of the product in opposed jet milling experiments (g)</td>
</tr>
<tr>
<td>( M_L )</td>
<td>Mass loss due to torrefaction (%)</td>
</tr>
<tr>
<td>( n )</td>
<td>Molar mass of air (mol)</td>
</tr>
<tr>
<td>( p )</td>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>( p_C )</td>
<td>Pressure of compressed grinding air (bar)</td>
</tr>
<tr>
<td>( p_{\text{UC}} )</td>
<td>Pressure of grinding air before compression (bar)</td>
</tr>
<tr>
<td>( Q^2 )</td>
<td>Cross-validated ( R^2 )</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>Coefficient of determination</td>
</tr>
<tr>
<td>( R^2(\text{Adj.}) )</td>
<td>Coefficient of determination adjusted for degrees of freedom</td>
</tr>
<tr>
<td>( R_8 )</td>
<td>Gas constant = 8.314 J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>( \text{SEC} )</td>
<td>Specific electrical energy consumption of the system (J g(^{-1}))</td>
</tr>
<tr>
<td>( \text{SEC}_{\text{JET}} )</td>
<td>Specific energy consumption based on the energy needed for compression of the grinding air in jet milling (J g(^{-1}))</td>
</tr>
<tr>
<td>( \text{SEC}_{\text{OSC}} )</td>
<td>Specific energy consumption based on the estimated total available impact energy of the grinding ball in oscillatory ball milling (J g(^{-1}))</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature of air (K)</td>
</tr>
<tr>
<td>( t )</td>
<td>Milling time (s)</td>
</tr>
<tr>
<td>( V )</td>
<td>Volume of air (m(^3))</td>
</tr>
<tr>
<td>( V_C )</td>
<td>Volume of compressed grinding air (m(^3))</td>
</tr>
</tbody>
</table>
\( V_{UC} \)  Volume of grinding air before compression (m³)
\( \Delta^* \)  Width of particle size distribution
\( \Delta_{AR} \)  Width of aspect ratio distribution
\( \Delta W_p \)  Work done by a piston in isothermal and quasistatic compression of an ideal gas (J)
\( \rho \)  Density of air (g m⁻³)
\( \sigma \)  Stress (MPa)
\( \sigma_C \)  Crushing strength or peak stress in compression (MPa)
\( \sigma_u \)  Ultimate strength (MPa)
List of original publications

This thesis is based on the following publications, which are referred throughout the text by their Roman numerals:


All the manuscripts were written by the primary author of this thesis, whose main responsibilities were experimental design, data analysing, modelling and reporting of the results. The co-authors participated in the design, analyses and writing of the publications.
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1 Introduction

1.1 Background

Wood is a renewable, abundant, non-food and carbon dioxide-neutral raw material that can be used to replace non-renewable materials. Wood is widely used as a fuel, construction material or raw material in cellulose and lignocellulose-based products. Today there are various applications in which wood is used in powdered form, such as thermoplastics and filters, and a lot of research effort has been put into developing novel ways of utilising wood powders (Kobayashi et al. 2008, Mori 2009).


Although the fine grinding of wood has been studied in various ways, see Millett et al. (1979), Fukazawa et al. (1982) and Agarwal et al. (2013), the main subject under study have been the application of wood powder, not the mechanical processing itself. Thus our present understanding of the process does not extend to the effects of fine grinding conditions on the particle morphology and cellulose crystallinity, which makes it very difficult to design and optimise processes for the fine grinding of wood for different applications. The general aim...
of this thesis is to obtain a knowledge of how the physical properties of Norway spruce (*Picea abies*) wood develop during dry fine grinding with impact-based mills under a variety of grinding conditions, and what influence those conditions have on energy consumption.

### 1.2 Outline of the thesis

This thesis is organised into six chapters. Chapter 1 presents a brief background to the topic. Chapter 2 summarises our present understanding of the structure and properties of Norway spruce wood and the milling of wood, especially dry fine grinding. The aims of the present research are presented in Chapter 3 and the materials and methods used for testing the hypotheses in Chapter 4. The results are summarised and discussed in Chapter 5 and the conclusions are presented in Chapter 6.
Table 1. Energy requirements of different milling techniques in the dry grinding of wood to a product size of less than 2 mm. Pilot-scale milling experiments are marked (pilot). The energy requirement can be specified either for the milling equipment (mill) or for the whole process (process).

<table>
<thead>
<tr>
<th>Milling technique</th>
<th>Raw material</th>
<th>Feed size</th>
<th>Product size</th>
<th>Energy requirement</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotating knife mill</td>
<td>Unspecified hardwood</td>
<td>$d_{5,100} = 22.40$ mm</td>
<td>$d_{5,100} = 1.60$ mm</td>
<td>130.0 kWh t$^{-1}$</td>
<td>Gadoche &amp; López 1989</td>
</tr>
<tr>
<td>Hammer mill</td>
<td>Unspecified hardwood</td>
<td>$d_{5,50} = 8^a$ mm</td>
<td>$d_{5,50} = 1$ mm</td>
<td>89.1 kWh t$^{-1}$</td>
<td>Esteban &amp; Carrasco 2006</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Poplar chips</td>
<td>$d_{S,50} = 8^a$ mm</td>
<td>$d_{S,50} = 1$ mm</td>
<td>113.2 kWh t$^{-1}$</td>
<td>Esteban &amp; Carrasco 2006</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Pine chips</td>
<td>-</td>
<td>$d_{S,44} = 1$ mm</td>
<td>102 kWh t$^{-1}$</td>
<td>Schell &amp; Harwood 1994</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Hybrid poplar wood chips</td>
<td>-</td>
<td>$d_{S,44} = 1$ mm</td>
<td>102 kWh t$^{-1}$</td>
<td>Schell &amp; Harwood 1994</td>
</tr>
<tr>
<td>Vibration mill</td>
<td>Norway spruce</td>
<td>$d = 22$ mm</td>
<td>$d = 150$ µm</td>
<td>800 kWh t$^{-1}$</td>
<td>Kobayashi et al. 2008</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Dry aspen wood chips</td>
<td>$d_{S,50} = 1.4$ mm</td>
<td>$d_{S,50} = 870$ µm</td>
<td>310* kWh t$^{-1}$</td>
<td>Gravelsins 1998</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Moist aspen wood chips</td>
<td>$d_{S,50} = 1.4$ mm</td>
<td>$d_{S,50} = 1.54$ mm</td>
<td>200* kWh t$^{-1}$</td>
<td>Gravelsins 1998</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Dry jack pine sawdust</td>
<td>$d_{S,50} = 2.2$ mm</td>
<td>$d_{S,50} = 970$ µm</td>
<td>78 kWh t$^{-1}$</td>
<td>Gravelsins 1998</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Moist jack pine sawdust</td>
<td>$d_{S,50} = 2.5$ mm</td>
<td>$d_{S,50} = 1.76$ mm</td>
<td>100* kWh t$^{-1}$</td>
<td>Gravelsins 1998</td>
</tr>
<tr>
<td>Disc mill</td>
<td>Hybrid poplar wood chips</td>
<td>-</td>
<td>$d_{S,50} = 1.2^a$ mm</td>
<td>122 kWh t$^{-1}$</td>
<td>Schell &amp; Harwood 1994</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Spruce</td>
<td>Sieved to</td>
<td>$d_{S,50} = 197$ µm</td>
<td>750 kWh t$^{-1}$</td>
<td>Repellin et al. 2010</td>
</tr>
<tr>
<td>(pilot)</td>
<td>Torrefied spruce</td>
<td>Sieved to</td>
<td>$d_{S,50} = 59$ µm</td>
<td>90* kWh t$^{-1}$</td>
<td>Repellin et al. 2010</td>
</tr>
</tbody>
</table>

$d_{S,X}$ = sieve aperture with X% material pass, $d_{50}$ = median particle diameter obtained by the laser diffraction technique, $d$ = particle diameter without no precise information provided in the source, MC = moisture content in relation to total mass, MC* = moisture content with the relation to total mass or dry mass not specified, ^a value read off from a graph and therefore not precise, ^b measuring method not mentioned, and ^c obtained by sieving of dry wood chips
2 Present understanding

2.1 Norway spruce wood

Among the various wood species, Norway spruce (*Picea abies* [L.] H. Karst) was chosen for this work because its properties and structure are well known and it is an important natural resource in Germany, Austria, Slovakia, the Czech Republic, Romania and the Scandinavian countries (Surmiński 2007). This section focuses on the structure and mechanical properties of mature Norway spruce wood, whereas the differences between trees grown in different surroundings or under different nutritional conditions are not considered in detail.

2.1.1 Chemical composition and microstructure

The chemical composition of Norway spruce wood includes primarily cellulose (> 39%) and lignin (< 36%) but also hemicelluloses and pectins (< 28%) (Bertraud & Holmbom 2004, Surmiński 2007). Its microstructure comprises mainly longitudinal cells, known as tracheids (up to 90%), the remainder being mainly the cells forming wood rays (Hejnowicz 2007). An illustration of a cross-section of a Norway spruce tree is provided in Fig. 1. Norway spruce tracheids are elongated cells and have sometimes been described as hollow tubes of length varying between 1.0 mm and 7.6 mm (Buksnowitz *et al.* 2010). Tracheid length varies depending on characteristics such as the age of the tree and the radial distance from the pith (Herman *et al.* 1998, Sarén *et al.* 2001, Buksnowitz *et al.* 2010). The cross-section of a tracheid is approximately rectangular, including an open space known as the lumen (Sarén *et al.* 2001, 2006, Derome *et al.* 2012). The length of the side of a tracheid seen in cross-section is less than 50 µm (Havimo *et al.* 2008), and the cell wall thickness can vary between 1 µm and 9 µm (Havimo *et al.* 2008, Derome *et al.* 2012). The average cell wall thickness is 2.1 µm in earlywood and 3.9 µm in latewood (Havimo *et al.* 2008). The latewood occupies from 2% to 30% of the total growth ring thickness (Hejnowicz 2007). The walls of the tracheids contain bordered pits between 11 µm and 22 µm in diameter (Hejnowicz 2007). These are mainly located in the radial walls of the earlywood and are abundant at the overlapping ends of the tracheids (Hejnowicz 2007).
Fig. 1. Illustration of a cross-section of a tree. L denotes longitudinal axis, R radial axis and T tangential axis.

Structure of tracheids

Tracheids are composed of a compound middle lamella (CML) and secondary cell wall layers $S_1$, $S_2$ and $S_3$, where the $S_2$ layer comprises 80% of the entire width of the secondary wall (Hejnowicz 2007). The CML, which contains a relatively high amount of lignin but low amounts of cellulose and hemicelluloses (Jääskeläinen & Sundqvist 2007: 50–51), can be separated into the middle lamella (ML) and primary wall layer (P) (Jääskeläinen & Sundqvist 2007: 50–51). The ML binds the tracheids to each other (Jääskeläinen & Sundqvist 2007: 50–51). The cell wall of a tracheid is made up of a primary wall layer and the secondary wall layers, where P is the outermost layer and $S_3$ the innermost (Jääskeläinen & Sundqvist 2007: 50–51). The wall layers differ from others by virtue of the orientation of the cellulose fibrils, as shown in Fig. 2. The angle between the cellulose fibrils and the longitudinal axis is called the microfibrillar angle (MFA). Earlywood tracheids exhibit an asymmetrical MFA distribution with values between -20° and 90° (Peura et al. 2008a). There are certain differences in MFA between the cell wall layers, and also within a single cell wall layer, as shown in the cell wall models (see Fig. 2). The average MFA tends to be between 20° and 35° near the pith and decreases to below 20° towards the bark (Sarén et al. 2001, 2006, Peura et al. 2008a, 2008b). It also tends to decrease within a single growth ring when moving from the earlywood towards the latewood (Sarén et al. 2006, Lanvermann et al. 2013). Likewise the relative distribution of cellulose, hemicelluloses and lignin is known to vary between the cell wall layers (Panshin & de Zeeuw 1980: 106–107). According to Fengel and Stoll (1973), the thicknesses of the cell wall layers lie in the range of 0.04–0.16 µm for CML, 0.12–0.71 µm for $S_1$, 0.91–5.60 µm for $S_2$ and 0.01–0.36 µm for $S_3$. 

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Cell wall structure of tracheids

In the cell walls of tracheids the cellulose molecules form the helically wound reinforcing fibrils whereas the hemicelluloses and lignin provide a gluing and stiffening matrix (Booker & Sell 1998). Besides the orientation of microfibrils in a cell wall of wood also hemicelluloses and lignin can form orientated molecular structures (Stevanic & Salmén 2009, Salmén et al. 2012). An elementary cellulose fibril of native wood consists of 10 000 glucose units of length around 5.2 µm, arranged so that they form a well-ordered crystalline structure or less ordered amorphous mass (Jääskeläinen & Sundqvist 2007: 67–71, Fengel & Wegener 1989: 66–105). In Norway spruce earlywood 52% (± 3%) of the cellulose by mass is in crystalline form (Andersson et al. 2004) and 30% (± 4%) of the wood by mass is composed of crystalline cellulose (Andersson et al. 2004), or an even lower proportion near the pith (Andersson et al. 2003). Jakob et al. (1995) report that an elementary cellulose fibril in the S2 layer of Norway spruce wood is uniformly 2.5 nm (± 0.2 nm) in diameter and is made up entirely of cellulose crystallites. The crystallites oriented along the fibre axis in the S2 layer have been reported to be 11 nm in length (Jakob et al. 1995). On the other hand, the average length and diameter of cellulose crystallites in the S2 layer of Norway spruce wood have been reported by Pirkkalainen et al. (2012) to be 33 nm (± 1 nm) and
2.7 nm (± 0.1 nm), respectively, values that are fairly close to those reported by Andersson et al. (2003) and Peura et al. (2008a). Peura et al. (2008a) concluded that the length of the cellulose crystallites can vary from 19.2 nm to 28.4 nm. Some authors have suggested that there are no systematic variations in crystallite dimensions as a function of the number of annual rings from the pith (Andersson et al. 2003, Pirkkalainen et al. 2012). In contrast to this, Peura et al. (2007, 2008a) reported that there are small differences in the thickness and length of crystallites between juvenile and mature wood. Individual elementary cellulose fibrils in the S2 layer of Norway spruce wood together with some hemicellulose glucomannan form cellulose fibril aggregates called macrofibrils with sides ranging in length from 5 nm to 25 nm, averaging 15–16 nm, assuming a square cross-section (Fahlén 2005). The centres of the elementary fibrils have been estimated to be 4 nm apart (Jakob et al. 1996). The macrofibrils are surrounded by lignin and hemicelluloses known as xylan and glucomannan (Fahlén 2005: 10). An illustration of an elementary cellulose fibril and macrofibrils in the S2 wall layer of Norway spruce wood is presented in Fig. 3.

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**Fig. 3. Illustrations of an elementary cellulose fibril and macrofibrils of various sizes in the S2 cell wall layer of Norway spruce.**
2.1.2 Mechanical properties and breakage behaviour

In mechanical terms, Norway spruce wood is a viscoelastic material (Havimo 2010), the viscous behaviour causes internal friction which converts any mechanical energy imposed on it into heat (Eskelinen et al. 1982, Havimo 2009). It also exhibits linear stress-strain behaviour when exposed to low magnitude stresses, but when exposed to stresses of magnitudes close to its ultimate strength, i.e. its breaking strength, non-linear stress-strain behaviour prevails (Dahl 2009). The mechanical properties of Norway spruce wood vary depending on the loading direction (Dahl 2009) and on structural variations such as the presence or absence of early- and latewood and differences in MFA (Reiterer et al. 1999, Reiterer et al. 2001a, Eder et al. 2008, 2009). Wood can be generally simplified as orthotropic, i.e. by considering the mechanical differences in its radial, longitudinal and tangential directions.

Fracture mechanics and breakage behaviour

In fracture mechanics of wood it is typical to distinguish three modes of loading that lead to different forms of failure behaviour (Fig. 4). Frühmann et al. (2002) have shown that pure tension failure can be more favoured energetically than pure shear failure in Norway spruce wood. One reason for this may be energy losses caused by friction between the fractured surfaces brought about by shear loads (Frühmann et al. 2002). On the other hand, mixed mode loading (modes I and II) can lead to failure that is energetically more favourable than pure tension failure (Tschegg et al. 2001), since in this type the initial crack propagation always takes place along the longitudinal axis irrespective of the starting notch or the degree of mixity (Jernkvist 2001).
The breakage of wood can occur due to the separation of cells from each other by peeling (intercellular failure), in which case the crack propagates mainly via the CML (Boatright & Garrett 1983, Ashby et al. 1985). It is also possible that breakage can occur within the cell wall layer (intracellular failure) (Boatright & Garrett 1983, Ashby et al. 1985), leading to either intrawall failure, i.e. failure within the secondary cell wall, or transwall failure, in which the fracture path intersects the cell wall (Côté & Hanna 1983). Tensile stressing experiments with Norway spruce wood have shown that fracturing mainly takes place in an intercellular or intrawall manner when the stresses are perpendicular to the longitudinal axis (Persson 2000: 46–51, Dill-Langer et al. 2002, Frühmann et al. 2003a, Wittel et al. 2005, Keunecke et al. 2007, Lanvermann et al. 2014), whereas transwall failure takes place when there is tension along the longitudinal axis (Bodner et al. 1997, 1998, Frühmann et al. 2003b, Müller et al. 2003). When tension is perpendicular to the longitudinal axis stresses in excess of 1 MPa but significantly less than 10 MPa are needed for breakage (Dill-Langer et al. 2002, Wittel et al. 2005, Dahl 2009, Lanvermann et al. 2014), whereas if the tension is parallel to the longitudinal axis over 30 MPa is needed for breakage of the wood (Dahl 2009) or of a single tracheid (Eder et al. 2009). The stressed area in experiments with wood samples is typically calculated as the whole area of the cross-section in which the failure takes place. This results in lower ultimate strengths by comparison with calculations that consider only the cross-section area of the cell wall, so that the open space represented by the lumen is excluded. When the latter calculation method is used local longitudinal ultimate tensile strengths may be obtained that are significantly over 200 MPa (Burgert et al. 2003, 2005, Eder et al. 2008, 2009), i.e. strengths of this magnitude need to be exceeded locally to cause transwall failure in single tracheids. There is no
information about the tensile loading of single tracheids in a tangential or radial direction as their dimensions are too small for the tensile testing equipment (Eder et al. 2013). In the case of shear experiments, stresses over 0.8 MPa but less than 9 MPa are sufficient to cause in-plane shear failures in different loading directions (Dahl 2009). Dahl (2009) reported that in the case of samples where the shear loading was initially directed to cause crack propagation across the longitudinal axis the crack did not propagate in this direction but along the longitudinal axis. Thus the shear stresses reported by Dahl (2009) do not consider the ultimate shear strength required for transwall failure in Norway spruce wood. By considering only the cross-section area of the cell wall in the calculations Gindl & Teischinger (2002) estimated the shear strength of the cell wall parallel to the longitudinal axis to be 27.5 MPa, i.e. this figure needs to be exceeded locally for intrawall shear failure.

**Compression failure**

During compression the breakage of wood takes place due to tension and shear failures but is accompanied by plastic deformation of its cells, i.e. buckling and collapsing (Dumail & Salmén 1996, Poulsen et al. 1997, Persson 2000: 46–51, Reiterer & Stanzl-Tschegg 2001b, Gindl and Teischinger 2002, De Magistris & Salmén 2005, Benabou 2008, 2010). Typical stress-strain curves for Norway spruce wood in the case of radial, tangential and longitudinal compression are illustrated in Fig. 5. The stress-strain curves shown in Fig. 5 have some general characteristics that have been distinguished for wood under compression (see Gibson and Ashby 1988: 283–290, 309–311). At low stresses linear-elastic deformation prevails, but when the stress increases to come close to the peak stress plastic deformation and failures take place (Gibson and Ashby 1988: 283–290, 309–311). The plateaux of the stress-strain curves correspond to a progressive crushing of the wood, involving plastic deformation, during which a significant increase in density is observed due to collapsing of the cells, allowing the denser wood to resist compression, as can be observed in the stress-strain curve in the form of strain toughening (Gibson and Ashby 1988: 283–290, 309–311). The increase in strength due to densification by compression nevertheless remains lower than could be expected from the increased density alone (Blomberg et al. 2005). The mechanical strength involved in compression is typically reported as taking the form of crushing strength, or peak stress, as illustrated in Fig. 5 for the longitudinal, radial and tangential compression curves.
The crushing strengths of spruce wood are listed in Table 2, where it can be seen that the crushing strength is much higher in a longitudinal direction than in any other direction and that in addition to density, the compression rate and moisture content have a significant influence on the crushing strength.

Apart from single static loading, cyclic compressive loading in tangential and radial directions with low applied stresses (0.5–0.7 MPa) can cause local collapsing of the earlywood and is particularly concentrated on the surface of the wood that is in contact with the compressive force (Salmi et al. 2009, 2012a, 2012b). When considering cyclic compression in a longitudinal direction, Clorius et al. (2000) reported that the fatigue life in wood is highly dependent on the loading frequency, in that the total time to failure decreases with increasing frequency. Visual failure was observed in the form of either a fine-meshed pattern of compression zones scattered over a larger section or else localised failure (Clorius et al. 2000). The fine-meshed failures increased with decreasing loading frequency and increasing moisture content (Clorius et al. 2000).

**Fig. 5.** Illustration of a typical stress-strain curves for Norway spruce wood under tangential, radial and longitudinal compression.
Table 2. Crushing strength of spruce wood under single compression. Values including an asterisk (*) were read off from a graph and are therefore not precise. Otherwise crushing strength is reported in terms of mean values. Bolded values apply to Norway spruce wood, whereas Widehammar (2004) did not specify the species of wood.

<table>
<thead>
<tr>
<th>Loading direction</th>
<th>MC Density (g cm(^{-3}))</th>
<th>Compression rate</th>
<th>Crushing strength/Peak stress (\sigma_C) (MPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Longitudinal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>‘Oven-dry’</td>
<td>low/medium/high</td>
<td>90° / 130° / 160°*</td>
<td>47.4±2.4</td>
<td>(Widehammar 2004)</td>
</tr>
<tr>
<td>8%</td>
<td>0.40</td>
<td>5.0 mm min(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12%</td>
<td>0.41</td>
<td>0.3 mm min(^{-1})</td>
<td>45</td>
<td>(Poulsen et al. 1997)</td>
</tr>
<tr>
<td>12%</td>
<td>0.4–0.9*</td>
<td>0.5 mm min(^{-1})</td>
<td>30–110*</td>
<td>(Gindl &amp; Teischinger 2002)</td>
</tr>
<tr>
<td>12–13%</td>
<td>0.40–0.43</td>
<td>5.0 mm min(^{-1})</td>
<td>49*</td>
<td>(Reiterer &amp; Stanzl-Tschegg 2001b)</td>
</tr>
<tr>
<td>10–15%</td>
<td>0.42–0.48</td>
<td>(1.2 / 12000 / 180000 mm/min(^{-1})</td>
<td>40.2* / 51.8* / 56.0*</td>
<td>(Eisenacher et al. 2013)</td>
</tr>
<tr>
<td>‘Fiber S’</td>
<td>low/medium/high</td>
<td>30° / 39° / 56°</td>
<td></td>
<td>(Widehammar 2004)</td>
</tr>
<tr>
<td>‘Fully S’</td>
<td>low/medium/high</td>
<td>28° / 37° / 52°</td>
<td></td>
<td>(Widehammar 2004)</td>
</tr>
<tr>
<td><strong>Radial</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>‘Oven-dry’</td>
<td>low/medium/high</td>
<td>9° / 10° / 15°</td>
<td></td>
<td>(Widehammar 2004)</td>
</tr>
<tr>
<td>12–13</td>
<td>0.40–0.43</td>
<td>5.0 mm min(^{-1})</td>
<td>3.5*</td>
<td>(Reiterer &amp; Stanzl-Tschegg 2001b)</td>
</tr>
<tr>
<td>‘Fiber S’</td>
<td>low/medium/high</td>
<td>3.6° / 5.0° / 7.5°*</td>
<td></td>
<td>(Widehammar 2004)</td>
</tr>
<tr>
<td>‘Fiber S’</td>
<td>0.38–0.48</td>
<td>0.0025 s(^{-1}) / 25 s(^{-1})</td>
<td>2.4° / 3.8°</td>
<td>(Uhmeier &amp; Salmén 1996)</td>
</tr>
<tr>
<td>‘Fully S’</td>
<td>low/medium/high</td>
<td>2.8° / 6.0° / 11°*</td>
<td></td>
<td>(Widehammar 2004)</td>
</tr>
<tr>
<td>‘Fiber S’</td>
<td>0.38–0.48</td>
<td>0.0025 s(^{-1}) / 25 s(^{-1})</td>
<td>2.0° / 3.8°</td>
<td>(Uhmeier &amp; Salmén 1996)</td>
</tr>
<tr>
<td><strong>Tangential</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>‘Oven-dry’</td>
<td>low/medium/high</td>
<td>19° / 24° / 30°</td>
<td></td>
<td>(Widehammar 2004)</td>
</tr>
<tr>
<td>‘Fiber S’</td>
<td>low/medium/high</td>
<td>4.5° / 7.5° / 10°</td>
<td></td>
<td>(Widehammar 2004)</td>
</tr>
<tr>
<td>‘Fully S’</td>
<td>low/medium/high</td>
<td>4.0° / 11° / 16°*</td>
<td></td>
<td>(Widehammar 2004)</td>
</tr>
</tbody>
</table>

\(^{*}\)Fiber S’ means fibre-saturated conditions in the wood, which in the case of Norway spruce is 30–34\% on a dry basis and 23–25\% on a wet basis. ‘Fully S’ means a condition of the wood in which it carries as much water as possible. Low/medium/high represent different strain rates in the split Hopkinson pressure bar (SHPB) experiments, although the strain rate cannot be prescribed accurately due to the testing technique. \(^{a}\) Lateral dilation of the samples was constrained during compression.
Influence of moisture content

Moisture content has a significant influence on the mechanical and fracture properties of wood (Gerhards 1982, Eskelinen et al. 1982, Salmén 1982, Bengtsson 2000, Vasic & Stanzl-Tschegg 2007). When the moisture of wood increases beyond the fibre saturation point (FSP), which varies between 30% and 34% on a dry basis and between 23% and 25% on a wet basis, the cell walls cease swelling because they are totally saturated and the timber strength no longer varies with moisture content (Bosshard 1974: 214, Berry & Roderick 2005). The energy loss due internal friction is significantly higher for water-saturated Norway spruce wood than for air-dried samples, even at temperatures below 30°C (Eskelinen et al. 1982).

Moisture content also has a significant effect on the glass transition point of amorphous cellulose, hemicelluloses and lignin (Jääskeläinen & Sundqvist 2007: 127–130). The polymer changes its physical state from a glass-like brittle material to a rubber-like viscous material when the temperature increases beyond the glass transition point (Salmén 1982, Jääskeläinen & Sundqvist 2007: 127–130). This point occurs around 200°C in hemicelluloses, amorphous cellulose and lignin in a dry state (Salmén 1982, Jääskeläinen & Sundqvist 2007: 127–130), but when the moisture content of the wood increases hydrophilic hemicelluloses can be softened at room temperatures (approximately 20°C) (Salmén 1982, 2004). A higher moisture content will also lower the glass transition point of lignin and amorphous cellulose, but these do not soften at room temperature (Salmén 2004, Jääskeläinen & Sundqvist 2007: 127–130). In mechanical pulping the stressing frequency also influences the softening temperature of the wood (Salmén et al. 1999).

2.2 Dry fine grinding

In mineral processing, grinding is the last stage in mechanical size reduction and is performed using mills of various kinds after the crushing stage (Bernotat & Schönert 2000, Wills 2006). It is sometimes referred as milling and is also commonly separated into two processes, wet and dry grinding. According to Lowrison (1974: 103–108) wet grinding typically means the grinding of a material containing about 50% of liquid by volume in the uncombined state. The present work will consider only dry grinding processes. Jankovic (2003) separates grinding as used in mineral processing into four subcategories based on the
particle size of the product: conventional grinding, regrinding, fine grinding and very fine grinding. Other subcategories to be found in the literature include coarse, superfine and ultrafine grinding (Lowrison 1974: 60, 115, Orumwense & Forssberg 1992, Jankovic 2003, Wang & Forssberg 2007, Zhao et al. 2009, Barakat et al. 2013). There are some differences between authors, however, in the product size ranges implied by these terms, so that fine grinding, for example, has been classified as reduction to a particle size range of 125–1000 µm by Lowrison (1974: 60), 100–1000 µm by Hukki (Lowrison 1974: 115), 200–600 µm by Taggart (Lowrison 1974: 115) and 10–30 µm by Jankovic (2003). Barakat et al. (2013) categorised the fine grinding of lignocellulosic biomasses to product size range less than 100 µm, which is used as the targeted median particle size of the product in this work.

2.2.1 Stressing conditions and material properties

To describe the material breakage achieved by different forms of size reduction equipment it is convenient to evaluate our knowledge of this breakage in terms of stressing conditions (Rumpf 1990: 103–114). This would make it possible to evaluate the breakage mechanism involved when changing the size reduction equipment, the physical conditions or the nature of the material. Peukert and Vogel (2001) developed a processing model which distinguishes between material properties and stressing conditions. Material function includes the information about breakage rate and breakage function, which are in turn dependent on the stressing conditions and stressing history that the particle has experienced (Peukert 2004). The stressing conditions as such are considered in the role of a machine function which comprises the type of size reduction equipment and the conditions of operation (Peukert and Vogel 2001).

Material function

When considering a material function it must be noted that there are various differences between the mechanical properties of materials. Even a single particle may contain regions with different ultimate strengths, and crack propagation during loading will probably take place in a region where the ultimate strength is the same or lower than the stress applied (Fig. 6). Crack propagation fatigue can take place even when the stress is insignificant, and this can weaken the material so that the maximum stress or energy that is required for failure in the next
stressing event is lowered (Scott-Emuakpor 2007, Campbell 2012). Breakage of the material does not necessarily happen at the strain rate equivalent to the ultimate strength (Fig. 7a), as it only takes place when the strain energy density is sufficient for the breakage (Fig. 7b) (ASM International 2003: 205, Jenkins & Khanna 2005: 209–211). Chemical and physical treatments can be used prior to mechanical size reduction to weaken the particle structure.

**Machine function**

A machine function involves three main parameters: stress intensity, stress number and stress type (Peukert and Vogel 2001, Peukert 2003, 2004). According to Peukert (2013), stress intensity should properly be termed stress energy, the energy transferred to the particle upon stressing. The stress number, or frequency, then indicates how many stress events take place during a certain period of time in the course of mechanical size reduction (Bernotat & Schönert 2000, Peukert and Vogel 2001, Peukert 2003, 2004). The third parameter, stress type, refers to the type of applied stress (Bernotat & Schönert 2000, Peukert and Vogel 2001, Peukert 2003, 2004). Compressive stresses are applied by compression or impact, which can cause breakdown of the initial particles to smaller ones (Wills 2006, Ennis et al. 2008), while shear stresses are typically applied by abrasive or cutting techniques (Ennis et al. 2008, Lowrison 1974: 255–260). Other machine functions include physical conditions such as the processing temperature and pressure, which can have a significant influence on the breakage behaviour of the particles.
Fig. 6. Illustration of a heterogeneous particle breakage under compressive loading at varying compressive stresses. It is assumed that the stress is maintained for as long as is needed for breakage to occur independently of the strain.
Fig. 7. Illustrations of different stress-strain curves a) with breaking points and ultimate strengths and b) the blue (Fig 7a) stress-strain curve under different stressing conditions.

Mill and product related stressing models

Kwade (2003) make a distinction between mill and product related stressing models, in which the stressing conditions are considered from different points of view. In the mill related stressing model the mechanical size reduction behaviour of a mill is characterised by the type of the stress events, the number of such events produced in the mill per unit time and the stress energy, which is the magnitude of the energy that can be supplied to the product particle by the mill in each stress event (Kwade 2003). In the product related stressing model, the result in terms of the mechanical size reduction is determined by the type of stress, the absolute number of stress events acting on one feed particle and the magnitude of the specific energy or specific force during each stress event (Kwade 2003).

2.2.2 Single and double impacts

Single-particle breakage tests are used to study material behaviour under conditions of slow compression and impact (Rumpf 1973, 1990: 108–114, Tavares 2007), whereas abrasive failure has its own branch of science, called tribology (see ASM International 2003: 259–266). Single-particle breakage tests involve three main loading methods that result in outcomes of different kinds: single impact, double impact and slow compression (Tavares 2007). In the first case the particle is loaded by impact with one contact point (Fig. 8a), in the second there are two or more contact points (Fig. 8b) and in slow compression the particle is compressed between two planes (Fig. 8c). Special kinds of impact testers can also be used in relation to mechanical pulping, e.g. where movement is
restricted at one end of the particle and the impacting device hits the other end (Fig. 8d) (Eskelinen et al. 1982, Marton & Eskelinen 1982, Berg 2001). In this case the directions of the forces applied to the particle during impact are similar to the directions of those applied in shear failure (see Section 2.1.2), so that this impact type will be referred to as shearing impact in the present work. Single-particle breakage tests have been used to obtain knowledge about material breakage behaviour under different loading conditions which can be used to predict milling behaviour (Vogel & Peukert 2002, 2003, 2004, 2005, Meier et al. 2008, 2009). Stressing conditions can also be utilised directly in milling, for example the mathematical expression for stressing conditions in stirred media milling evaluated by Kwade et al. (1996) is nowadays being used in many studies aimed at the optimisation of stirred media milling.

Fig. 8. Illustrations of different stress types: a) single impact, b) double impact, c) slow compression and d) shearing impact. In the figure $v_{\text{PARTICLE}}$ is the particle velocity, $v_{\text{BALL}}$ the grinding ball velocity, $\omega_1$ the angular velocity of the roll 1, $\omega_2$ the angular velocity of roll 2 and $v_{\text{HAMMER}}$ the velocity of the impacting hammer.

Single particle tests have been used to obtain knowledge in relation to wood construction and mechanical pulping. The crushing strength of wood is significantly higher when it is exposed to a single or double impact than in typical compression tests (Reid & Peng 1997, Pierre et al. 2013). With double impacts, for instance, the longitudinal crushing strength of Norway spruce wood increases approximately from 50 MPa to 70 MPa when the impact speed is increased from 0.001 m s$^{-1}$ to 3.0 m s$^{-1}$ (Neumann et al. 2011). Pierre et al. (2013) have reported that fibre and fully saturated spruce (Picea excelsa) and poplar (Populus euramericana) exhibit less fractured zones and a lower crushing strength than air-dried samples when imposed to double impacts at a speed of 1.7 m s$^{-1}$. As in double impact tests, the impact speed in the case of single impacts increases the crushing strength, but this effect has been found to be even more marked when the impact is imposed across the grain rather than along the grain (Reid & Peng 1997). The energy losses in a single impact are higher than in typical compression
tests (Reid & Peng 1997). Some of the kinetic energy carried by the specimens is converted to thermal energy and the work needed for the inelastic deformation during the impact event, but some is transferred back due to rebounding (Reid & Peng 1997). The deformation mechanism is more localised in single impact cases than in typical compression tests (Reid & Peng 1997), and disintegration of the specimen takes place near the targeted surface when the impact is along the grain, whereas when it is perpendicular to the grain the deformation propagates into the undeformed part of the specimen leaving the characteristic mushroom profile in the deformed part (Reid & Peng 1997). Shearing impact studies consider only the specimen orientations that cause fractures along the grain, because these are the most closely related to the behaviour of wood in mechanical pulping (Eskelinen et al. 1982, Marton & Eskelinen 1982, Berg 2001). Eskelinen et al. (1982) concluded that there is no significant difference in impact energy with respect to the direction of the fracture. The fracturing energy of Norway spruce wood in the case of radial shearing impacts can be up to four times larger than that in pure cleavage (Marton & Eskelinen 1982). Fracturing energy in shearing impact can also be affected by the impact velocity (Berg 2001).

2.2.3 Fine grinding techniques

Yokoyama & Inoue (2007) classified fine grinding mills into five groups: impact mills, ball media mills, air jet mills, roller mills and those of some other type. The mills classified in this scheme as impact mills could more conveniently be named rotor impact mills, as in the definition proposed by Nied (2007). In rotor impact mills the size reduction is achieved by single impacts, where the kinetic or impact energy being applied through the rotary movement of rotors (Nied 2007). Rotor impact mills with integrated classifiers are frequently referred to as classifier mills and can be used for producing the finest material of all the types of rotor impact mills, whereas typical hammer mills are used for the production of coarser material (Nied 2007). Classifiers are used to control the residence time distribution of the particle inside the milling zone, which correlates with the number of stress events (Peukert & Vogel 2001). Ball media mills are mills in which grinding media such as balls or beads are driven by movement of the mill casing or by an agitator (Yokoyama & Inoue 2007). These mills involve single impacts in which the grinding balls collide with particles, and also double impacts in which particles are caught between colliding grinding balls or between grinding balls and the mill casing. There are generally no restrictions on the use
of non-spherical grinding media in these mills, which is a good reason for referring to them as media mills or grinding media mills, as preferred by Ennis et al. (2008), Bernotat & Schönert (2000) and Orumwense & Forssberg (1992). An air jet mill is a fluid energy mill, or jet mill, that uses high velocity jets of air to impart energy to particles for size reduction (Chamayou & Dodds 2007). Besides air, nitrogen gas and steam can also be used as the fluid in such mills (Camayou & Dodds 2007). Jet mills can be further categorised as spiral, opposed, oval chamber and target jet mills (Camayou & Dodds 2007, Ennis et al. 2008). Yokoyama & Inoue (2007) have classified spiral and oval chamber jet mills as attrition type jet mills. Spiral jet mills are also known as pancake mills (Camayou & Dodds 2007). Fluidised bed opposed jet mills are ones in which air jets are used to provide high-energy single impacts between particles in a fluidised bed (Chamayou & Dodds 2007). Here the kinetic energy of the grinding air can be evaluated from the grinding pressure, which has a significant influence on the particle breakage mechanism (De Vegt 2007, Palaniandy et al. 2008, Palaniandy & Azizli 2009). Jet mills are typically employed in the last stage of the dry fine grinding process, to obtain the finest particles (Camayou & Dodds 2007, Yokoyama & Inoue 2007). Roller mills can be divided into mills that use a roller tumbling on a table or in a vessel (roller tumbling type) and those in which the feed is ground between cylindrical rolls (roll type) (Yokoyama & Inoue 2007). Roller mills with smooth roll profiles can be used to apply a fine grinding technique based on slow compression. The “mills of other types” include those which cannot be classified as rotor impact mills, grinding media mills, jet mills or roller mills, including those in which cutting tools such as knives, shears, saws and spikes are employed (Lorrison 1974: 255–260). Disc refiners or disc mills are the ones that are most commonly used for refining wood and cellulose, i.e. in mechanical pulping (Sundholm 1999, Tienvieri et al. 1999, Zhu JY 2011). In these a rotor provides the mechanical energy needed for size reduction, as in rotor impact mills, but due to their specific breakage mechanism designed to cause defibration and the fibrillation of fibres (Salmén et al. 1999), they are classified as “other mills” in the present scheme. Apart from disc refiners, grinding wheels operating under varying physical conditions are also used for mechanical pulping (Liimatainen et al. 1999, Sundholm 1999). Since the disc refiners and grinding wheels used in mechanical pulping have been optimised for the production of long fibres, their potential for fine grinding is poorly known. A summary of the classification of fine grinding mills is presented in Table 3.
Table 3. Classification of fine grinding mills based on suggestions by Orumwense & Forssberg (1992) and Yokoyama & Inoue (2007).

<table>
<thead>
<tr>
<th>Category</th>
<th>Technique</th>
<th>Mill types/models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Media mills</td>
<td></td>
<td>Tumbling type, vibration type, planetary type, centrifugal fluidised-bed type</td>
</tr>
<tr>
<td></td>
<td>Case driven</td>
<td>Tumbling type, vibration type, planetary type, centrifugal fluidised-bed type</td>
</tr>
<tr>
<td></td>
<td>Agitator driven</td>
<td>Tower type, agitation vessel type, tubular type, annular type</td>
</tr>
<tr>
<td>Non-media mills</td>
<td>Rotor impact mills</td>
<td>High-speed rotation disc type, hammer type, axial flow type, annular type</td>
</tr>
<tr>
<td></td>
<td>Jet mills</td>
<td>Target collision type, opposed jet type, attrition type</td>
</tr>
<tr>
<td></td>
<td>Roller mills</td>
<td>Roller tumbling type, roll type</td>
</tr>
<tr>
<td></td>
<td>Other mills</td>
<td>Cutting type, grinding wheel type, disc refiners, mortar and pestle</td>
</tr>
</tbody>
</table>

2.3 Impact milling of wood and other lignocelluloses

Impact milling is preferred for the mechanical size reduction of viscoelastic materials, and there are in principal three impact milling techniques that can be used for fine grinding purposes: opposed jet mills, high-speed rotor impact mills, and grinding media mills operated in the impacting mode. The impact events involved in these techniques are illustrated in Fig. 9.

![Fig. 9. Schematic illustration of the impact events involved in a) an opposed jet mill, b) a high-speed rotor impact mill, and c) an oscillatory ball mill, which is one kind of vibration mill. The mills are not illustrated to scale with respect to size. Paper II, published by permission of Elsevier.](image)

One way of distinguishing the breakage mechanisms in milling is to consider the developments in particle size, shape and cellulose crystallinity that occur during milling, all of which can be attributed to the mechanical properties of the wood. Changes in particle size, shape and cellulose crystallinity in Norway spruce wood subjected to different impact loading intensities are listed in Table 4 in relation to
breakage behaviour (see Section 2.1.2). Intensity I in Table 4 represents loading with stresses that are unable to cause fracturing in any direction by means of a single stressing event. Intensity II represents a single loading situation in Norway spruce wood in which interwall and intrawall failures can take place but transwall failures do not occur. Cracks propagate by means of the energetically most favoured path, which is along the grain, leaving the particles rather elongated in shape. The breakage behaviour of the wood particles at Intensity II is rather similar to the Class I breakage in the classification suggested by Leu & Zhu JY (2013). Intensity III can cause severe intracellular- and intercellular damage in early- and latewood independently of the loading direction, which leads to less elongated shapes than with Intensity II. Intensity IV represents an impact which is sufficient for the amorphisation of cellulose. According to Vincent (1990), the theoretical strength of crystalline cellulose is 25 GPa, which is many magnitudes higher than the stresses needed for transwall failures in tracheids (see Burgert et al. 2003, 2005, Eder et al. 2008, 2009). The breakage behaviour of wood particles at Intensities III and IV is rather similar to Class II breakage in the classification suggested by Leu & Zhu JY (2013). As the stressed area during particle size reduction may decrease as the particle size decreases, possibly resulting in higher local stress, the occurrence of Intensities I–IV in milling is influenced by the particle size range.
Table 4. Possible breakage behaviour due to differences in ultimate strength in Norway spruce wood when exposed to a single impact of different intensities, and its influence on the size, shape and relative degree of cellulose crystallinity.

<table>
<thead>
<tr>
<th>Impact intensity</th>
<th>Breakage behaviour</th>
<th>Changes in size, shape and cellulose crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (No failures)</td>
<td>- No breakage</td>
<td>- No changes</td>
</tr>
<tr>
<td></td>
<td>- Fatigues are possible</td>
<td></td>
</tr>
<tr>
<td>II (Intercellular and intrawall failures)</td>
<td>- Fractures depend on the orientation of the wood</td>
<td>- Particle size decreases but tracheids can remain 1–7 mm in size in a longitudinal direction</td>
</tr>
<tr>
<td></td>
<td>- Intercellular and intrawall failures in tracheids</td>
<td>- Shape changes but tracheids can remain elongated</td>
</tr>
<tr>
<td></td>
<td>- No transwall failures in tracheids</td>
<td>- No changes in relative degree of cellulose crystallinity</td>
</tr>
<tr>
<td></td>
<td>- Fatigues</td>
<td></td>
</tr>
<tr>
<td>III (Transwall failures)</td>
<td>- Fractures independent of the orientation of the wood</td>
<td>- Particle size decreases</td>
</tr>
<tr>
<td></td>
<td>- Intracellular and intercellular failures in tracheids</td>
<td>- Shape changes</td>
</tr>
<tr>
<td></td>
<td>- Fatigues</td>
<td>- No changes in relative degree of cellulose crystallinity</td>
</tr>
<tr>
<td>IV (Amorphisation of cellulose)</td>
<td>- Fractures independent of the orientation of the wood</td>
<td>- Particle size decreases</td>
</tr>
<tr>
<td></td>
<td>- Intracellular and intercellular failures in tracheids</td>
<td>- Shape changes</td>
</tr>
<tr>
<td></td>
<td>- Amorphisation of cellulose</td>
<td>- Relative degree of cellulose crystallinity decreases</td>
</tr>
<tr>
<td></td>
<td>- Fatigues</td>
<td></td>
</tr>
</tbody>
</table>

2.3.1 Mills involving single impacts

Rotor impact milling

Rotor impact mills can be used to grind wood to a median particle size well over 100 µm (Himmel et al. 1985, Gadoche & López 1989, Schell & Harwood 1994, Paulrud et al. 2002, Esteban & Carrasco 2006, Zhu JY et al. 2009a, Repellin et al. 2010). Integrated sieves or classifiers are used in rotor impact milling to control the fineness of the product (Nied 2007), but Schell & Harwood (1994) report that these are not recommended by hammer mill vendors for the milling of moist wood chips due to low production rates, excessive heat build-up, screen blinding
and equipment damage. Due to these problems in the processing of moist lignocelluloses, hammer mills are recommended only for the size reduction of lignocelluloses of a moisture content up to 10–15% on a wet basis (Kratky & Jirout 2011).

Rotor impact milled wood particles are considered to be more cylinder-like than spherical in shape (Zhu et al. 2009a). Paulrud et al. (2002) have shown that the size and shape of the wood particles are affected by the type of rotor impact mill, but more distinct differences in the properties of wood powders are evident when rotor impact milled wood is compared with cutting milled wood. Rotor impact milled wood particles are more elongated than cutting milled particles (Paulrud et al. 2002), but less elongated than those milled with a disc refiner with or without steam preheating (Schell & Harwood 1994).

There is no information on whether rotor impact milling can provide sufficient stress intensities to cause a decrease in the relative degree of cellulose crystallinity, nor is it known whether wood can be ground to a median particle size below 100 µm, which would involve significant destruction of the cell walls. Paper I in the present thesis investigates the dry fine grinding of Norway spruce wood with a high-speed rotor impact mill equipped with an integrated air classifier and considers the effect of the rotor and classifier speeds on the properties of the wood powders and specific energy consumption during the processing. Rotor speed is associated with the energy and intensity of the single impacts, whereas it is the classifier that controls the time spent in the milling zone, i.e. the number of impact events. The higher this number, the finer the product will be if the impact energy is sufficient to cause breakage.

**Opposed jet milling**

It has been shown for wheat straw that opposed jet milling can be used to produce very fine particles without any significant decrease in cellulose crystallinity (Silva et al. 2012). Significant differences in the degree of cellulose crystallinity were observed between jet milled and grinding media milled samples when the median particle size of the wheat straw was less than 100 µm (Silva et al. 2012).

There is no information on how opposed jet milling influences the physical properties of dry wood, especially when ground to a median particle size below 100 µm. This was investigated in Paper II using a fluidised opposed jet mill with an integrated classifier and varying the grinding pressure in order to obtain
different kinetic energies in the impacts and the classifier speed in order to alter the number of stress events.

2.3.2 Mills involving double impacts

Grinding media milling

By comparison with non-media mills, media mills are known for their ability to cause efficient destruction of the cell walls, leading to disappearance of the fibrous structure in the wood (Fukazawa et al. 1982, Maurer & Fengel 1992, Mikushina et al. 2003, Agarwal et al. 2013). According to Mikushina et al. (2003) the fibrous structure of air-dried aspen sawdust is destroyed more rapidly in planetary ball milling than in vibration or tumbling ball milling, where the latter is the slowest technique for this purpose. Besides efficient destruction of the fibrous structure, media mills are well known for their ability to reduce the cellulose crystallinity of the particles in order to obtain total amorphisation of the cellulose when milling wood and other lignocellulosic substances with a low moisture content (Pew & Weyna 1962, Millett et al. 1979, Rivers & Emert 1987, Hon 1987, Maurer & Fengel 1992, Stubičar et al. 1998, Kobayashi et al. 2007, da Silva et al. 2010, Zhang Q et al. 2011, Silva et al. 2012). Some authors have reported that a low moisture content in the wood is extremely important when it is necessary to reduce the relative degree of crystallinity of cellulose in grinding media milling (Millett et al. 1976, Kobayashi et al. 2007). Grinding media milling can also influence the macromolecular structure of the wood components, which can be seen as an increase in the water-soluble oligomer content, the formation of mechanoradicals and reductions in the degree of polymerisation of cellulose and lignin (Chang H et al. 1975, Hon & Glasser 1979, Hon 1987, Mikushina et al. 2002, Ikeda et al. 2002, Guerra et al. 2006). Mechanoradicals are formed on account of the cleavage of covalent bonds in lignin and cellulose (Hon 1987, Guerra et al. 2006).

Kobayashi et al. (2008) used vibration milling to reduce Norway spruce wood to a median particle size of 24 µm, producing rounded broken fibres with smooth surfaces and a significant decrease in the relative degree of cellulose crystallinity. According to Schwanninger et al. (2004) the decrease in cellulose crystallinity achieved during the vibration milling of Norway spruce wood is mainly due to the mechanical treatment, whereas temperature and chemical
effects are of only minor importance. The cell corners and CML of Norway spruce wood are the most resistant elements in vibration milling, while in the secondary cell wall layer it is the S$_1$ layer that is particularly sensitive and is loosened at an early stage, whereas the S$_2$ layer is split into lamellae of varying diameters from 10 nm to 500 nm (Maurer & Fengel 1992). Maurer & Fengel (1992) observed the presence of globular particles in powdered Norway spruce wood that tended to aggregate during vibration milling and increased in number with the prolongation of milling. In view of the proposal put forward by Nichols et al. (2002), the term “agglomeration” is used rather than “aggregation” for an assemblage of powder particles in this work. This agglomeration of globular particles may be the reason why Kobayashi et al. (2008) found that a prolongation of vibration milling from 30 min to 120 min increased the median particle size of ground Norway spruce wood from 30 µm to 45 µm.

The agglomeration that takes place in Norway spruce wood during vibration milling means that there is a certain median particle size range that imposes limitations on particle size reduction. This has not been confirmed, however, and it is not clear whether higher stress energies will help to reduce the particle size any further or will merely intensify the agglomeration. This was investigated in Paper III, where dried Norway spruce wood was pulverised with a simple vibration mill in which double impacts played an important role. The stress energy was varied by changing the mass of the grinding ball or its oscillation frequency. Milling time and oscillation frequency were used to adjust the number of stress events. It also remains unknown how high the moisture content can be without exercising any significant influence on the crystallinity of cellulose in grinding media milling. This was studied in Paper IV.

2.3.3 Pretreatments and milling conditions

There are various chemical, enzymatic and thermal pretreatments that have been applied prior to the mechanical size reduction of wood (Lindholm & Kurdin 1999, Kenealy & Jeffries 2003, Rapp et al. 2006, Laxman & Lachke 2009, Zhu JY et al. 2009a, 2009b, 2010a, Zhu JY & Pan 2010b, Zhu W et al. 2010). Thermal pretreatment temperatures from 50°C to 150°C are considered to lead to non-reactive drying, in which lignocelluloses lose moisture and shrink (Tumuluru et al. 2011). This dehydration can cause defects and cracks in the wood (Repellin et al. 2010). Temperature range from 150°C to 200°C is considered as the reactive drying range, which results in structural damage due to cell wall collapse, and
Correspondingly, temperatures from 200°C to 300°C are considered to constitute a destructive drying range, involving depolymerisation and devolatilisation (Tumuluru et al. 2011). Drying also affects cellulose crystallinity (Esteves & Pereira 2009, Leppänen et al. 2011). In terms of changes in Norway spruce wood at the cellular level, drying in a reduced oxygen atmosphere at temperatures up to 220°C has been found to cause deformation in the earlywood and tangential intracellular cracks in the latewood (Welzbacher et al. 2011).

Torrefaction is a thermal pretreatment applied at temperatures in the range from 200°C to 300°C in an inert atmosphere that alters the physical and chemical composition of a lignocellulose (Tumuluru et al. 2011, van der Stelt et al. 2011, Acharya et al. 2012, Broström et al. 2012). It has been shown that torrefaction can be used to reduce the specific energy requirement in the grinding of wood with various designs of mill in order to obtain the desired particle size (Arias et al. 2008, Repellin et al. 2010, Almendros et al. 2011, Phanphanich & Mani 2011, Chen W-H et al. 2011, Kokko et al. 2012, van Essendelft et al. 2013). The decrease in energy consumption correlates with the anhydrous weight loss due to torrefaction (Repellin et al. 2010, Kokko et al. 2012). The reason for this behaviour has been said to lie in the increased brittleness of the lignocellulose during torrefaction (Tumuluru et al. 2011, Acharya et al. 2012), but we have no information on whether torrefaction actually has any influence on grindability and cellulose crystallinity in grinding media milling to a median particle size below 100 µm. Another important question is whether torrefaction pretreatment weakens the structure so as to allow smaller particle sizes to be achieved. This was studied in Paper V using impact-based grinding media mill.

In the case of viscoelastic materials, cryogenic grinding is considered to be a more effective method for fine grinding purposes (Wilczek et al. 2004). In addition, cooling affects the movements of the molecules, so that plastic deformation by viscous flows is reduced (Wilczek et al. 2004). Cryogenic grinding conditions have been employed in the grinding media milling of wood (Hon & Glasser 1979, Hon 1987, Maurer & Fengel 1992), leading Maurer & Fengel (1992) to conclude that these conditions have no appreciable influence on milling intensity by comparison with atmospheric conditions. However, a reduction in temperature down to -196°C will promote a decrease in the ultimate strength of wood (Gerhards 1982, Jiang et al. 2014). Moisture content is also important, because a higher moisture content provides greater changes in ultimate strength when lowering the temperature (Gerhards 1982). On the other hand, when considering material with a high moisture content the use of processing
temperatures that are below the glass transition point of hemicelluloses will prevent softening of these (Jääskeläinen & Sundqvist 2007: 127–130). The moisture content of living trees is around 40–50%, and brittle behaviour is typically observed at temperatures below -40°C (Jääskeläinen & Sundqvist 2007: 16, 127–130). We have no information on how the size, shape and crystallinity of particles are affected by cryogenic processing conditions in fine grinding of wood samples of varying moisture content. This was studied in Paper IV for moisture content values between 1% and 50% on a wet basis. The fine grinding was performed with an impact-based grinding media mill that was tailored for cryogenic grinding.
3 Aims of the study

Wood powders have many interesting possible applications, but due to a lack of knowledge about the processes involved, their industrial production is looked on as ecologically unfeasible. The technology needed for dry fine grinding already exists, but we do not know how the properties of the wood develop during fine grinding and how the processing should be optimised to minimise the specific energy consumption. The general aim was to obtain information on how the physical properties of Norway spruce (*Picea abies*) wood develop during dry fine grinding with impact-based mills under varying sets of grinding conditions and what influence these have on energy consumption. The specific aims were to gain an understanding of:

1. developments in the size and shape of dried wood particles in fine grinding with impact mills (Papers I–III),
2. the influence of grinding conditions on specific energy consumption in the fine grinding of dried wood with impact mills (Papers I–III),
3. the influence of cryogenic milling conditions and the drying of fresh wood on the size, shape and cellulose crystallinity of wood particles in fine grinding with double impact mills (Paper IV), and
4. the influence of mild torrefaction on the grindability, particle shape and cellulose crystallinity of dried wood in fine grinding with double impact mills (Paper V).
4 Materials and methods

4.1 Raw material

Norway spruce *Picea abies* (L.) H. Karst trees were harvested mainly from the southern parts of Finland. The harvested trees were debarked and processed with a circular saw at the Seikun Saha sawmill (Pori, Finland). The fresh sawdust was gathered from the circular saw process and sent to the University of Oulu, where it was stored in a freezer prior to the fine grinding experiments.

4.2 Pretreatments prior to fine grinding

The sawdust was screened and usually dried before the fine grinding experiments. Fresh sawdust was used only in the experiments presented in Paper IV. Drying took place in a large oven at non-reactive drying temperatures of 80°C (Papers III and IV) and 105°C (Papers I, II, V). The dry matter content after drying was measured with an MA100 moisture analyser (Sartorius AG, Germany). The moisture content values listed in Table 5 were calculated by deducting the measured dry matter content from 100%, and therefore represent the moisture content on a wet basis. Screening was performed with a vibratory sieve equipped with a screen having 4 mm circular holes. The particle size distribution of the screened and dried sawdust was measured with an Analysette 3 (Fritsch, Germany) vibratory sieve shaker in Paper I and with an e200LS (Hosokawa Alpine, Germany) air jet sieve in Paper III. The median particle size was between 1 mm and 2 mm, and less than 4% of the particles by weight passed through a sieve with an aperture of 250 µm in both cases. In Paper II the dried and screened Norway spruce was preground with the same air classifier mill as was used for the fine grinding in Paper I. This was a high-speed rotor impact mill 50 ZPS (Hosokawa Alpine, Germany) integrated in a closed grinding circuit with a 50 ATP air classifier (Hosokawa Alpine, Germany). After pregrinding, the finest particles were removed with the 50 ATP air classifier and the coarser particles were used as a feed in the fine grinding experiments. For Paper V several samples of dried and screened Norway spruce sawdust were torrefied in a nitrogen atmosphere at temperatures below 230°C before fine grinding.
Table 5. Drying temperatures and moisture content after drying.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Drying temperature (°C)</th>
<th>Moisture content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>105</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>II</td>
<td>105</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>III</td>
<td>80</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>IV</td>
<td>80</td>
<td>1–50</td>
</tr>
<tr>
<td>V</td>
<td>105</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

4.3 Fine grinding experiments

The fine grinding equipment, operational parameters, milling conditions and pretreatments used in the work reported in Papers I–V are listed in Table 6, and the differences in the impact angles used in the air classifier milling are illustrated in Fig. 10. The fine grinding experiments were performed under ambient milling conditions unless otherwise stated. Detailed experimental plans are presented in the original Papers I–V. For Paper I the air classifier mill was used for fine grinding and its specific energy consumption was calculated from the overall electricity consumption as presented in Paper I. For Paper II a fluidised bed opposed jet mill, 100 AFG (Hosokawa Alpine, Germany), and an oscillatory ball mill, Cryomill (Retsch, Germany), were used for fine grinding purposes. Like the air classifier mill, the jet mill was also integrated into a closed grinding circuit with the 50 ATP air classifier (Hosokawa Alpine, Germany).

The work done in compressing the grinding air in the jet milling experiments was calculated on the assumption that air behaves as an ideal gas and that compression is an isothermal process. The air was compressed by means of a GA11FF screw compressor (Atlas Copco, Italy), but for the purpose of the calculations the compression work was regarded as quasistatic and isothermal work done by a piston $\Delta W_P$ and calculated using the equation

$$\Delta W_P = nR_gT \ln \left( \frac{V_{UC}}{V_C} \right) = \frac{V_{UC}R_gT \rho}{M_{air}} \ln \left( \frac{p_C}{p_{UC}} \right),$$

where $n$ is the amount of the substance (air), $R_g$ the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ the air temperature, $V$ the volume of air, $M_{air}$ the molar mass of air, $\rho$ the density of air and $p$ the pressure of air. The subscript “C” in Equation 1 stands for the compressed air and “UC” for the uncompressed air.

The 100 AFG fluidised bed opposed jet mill contains built-in devices for measuring the classifier speed, pressure of the grinding air and total air flow rate,
data on which were collected during milling. The volume of the grinding air was measured with an SS 30.301 thermal inline flow sensor (Schmidt technology, Germany) connected to the pipe used to transfer the grinding air from the compressor to the jet mill. The temperature during the fine grinding experiments was approximately 293 K. The air volume in the SS 30.301 sensor was displayed and recorded as a normal volume (Nm³) which in this particular device is the volume at 20°C and 101,325 Pa according to the manufacturer. The dry mass of product, $m_{P,dry}$, was calculated by subtracting the dry mass of the wood that did not get past the classifier from the input dry mass. The specific energy consumption in jet milling SEC$_{JET}$ was calculated as

$$SE_{C_{JET}} = \frac{\Delta W_J}{m_{P,dry}}.$$  \hspace{1cm} (2)

Further information on the experiments is provided in Paper II.

In Paper III the fine grinding was studied with the oscillatory ball mill. For calculation of specific energy consumption in oscillatory ball milling there was estimated the total available impact energy of a single grinding ball $E_T$ (see Paper III). The total available impact energy was calculated as

$$E_T = SN_e \cdot E_k,$$  \hspace{1cm} (3)

where

$$SN_e = 2 \cdot f \cdot t,$$  \hspace{1cm} (4)

and

$$E_k = 8m_{ball} \cdot A^2 \cdot f^2,$$  \hspace{1cm} (5)

where in Equations 4 and 5 $f$ is oscillation frequency, $t$ milling time, $m_{ball}$ the mass of the grinding ball and $A$ the end-to-end amplitude of the oscillation. The specific energy in oscillatory ball milling SEC$_{OSC}$ was calculated as

$$EC_{OSC} = \frac{E_T}{m},$$  \hspace{1cm} (6)

where $m$ is the mass of the feed.

For the work described in Paper IV, fine grinding of screened Norway spruce sawdust samples of varying moisture content was performed using the oscillatory ball mill operated under ambient and cryogenic grinding conditions, using nitrogen liquid (boiling point -196°C) as a coolant. Similarly, the fine grinding of
dried, screened and torrefied Norway spruce sawdust reported in Paper V took place in the oscillatory ball mill. Torrefaction was performed in a nitrogen atmosphere and the mass losses due to torrefaction ($M_t$) were evaluated according to Almeida et al. (2010), the result being used to represent the intensity of torrefaction. The specific energy consumption as indicated in Paper V was calculated using Equation 6.

Table 6. Milling equipment and studied operational parameters, milling conditions and pretreatments.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Milling equipment</th>
<th>Mill type(s)</th>
<th>Studied operational parameters, milling conditions and pretreatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Air classifier mill: a Rotor impact mill 50 ZPS integrated with an air classifier 50 ATP (Hosokawa Alpine, Germany)</td>
<td>High-speed rotation disc type</td>
<td>Rotor/mill speed (50 ZPS), classifier speed (50 ATP), impact angle (50 ZPS)</td>
</tr>
<tr>
<td>II</td>
<td>Air classifier mill, a fluidised bed opposed jet mill 100 AFG integrated with the air classifier 50 ATP (Hosokawa Alpine, Germany) and an oscillatory ball mill CryoMill (Retsch, Germany)</td>
<td>High-speed rotation disc type, opposed jet type and vibration type</td>
<td>Grinding pressure (100 AFG), classifier speed (50 ATP)</td>
</tr>
<tr>
<td>III</td>
<td>Oscillatory ball mill CryoMill (Retsch, Germany)</td>
<td>Vibration type</td>
<td>Grinding ball mass, mass of the feed, oscillation frequency, milling time</td>
</tr>
<tr>
<td>IV</td>
<td>Oscillatory ball mill CryoMill (Retsch, Germany)</td>
<td>Vibration type</td>
<td>Cryogenic milling conditions, Moisture content of the feed</td>
</tr>
<tr>
<td>V</td>
<td>Oscillatory ball mill CryoMill (Retsch, Germany)</td>
<td>Vibration type</td>
<td>Torrefaction</td>
</tr>
</tbody>
</table>

Fig. 10. Impact angles studied in the air classifier milling experiments, referred to as "long edge" or I(long) and "short edge" or I(short). The black arrow indicates the rotation direction of the rotor.
The fine grinding experiments were replicated in most cases in order to obtain information about the uncertainty affecting the processing and analysing. In these cases the mean values were used for plotting and error bars were used to represent 95% confidence intervals when assuming a normal distribution. In the tables presented in Chapter 5 the results are expressed in the following form: mean value ± confidence interval.

4.4 Wood powder sampling and analyses

The measured properties of the pulverised Norway spruce wood samples as indicated in Papers I–V are listed in Table 7. Since their X-ray diffraction (XRD) profiles were measured in order to evaluate the crystallinity index, the measured XRD profiles are not shown in Papers I, II and V.

<table>
<thead>
<tr>
<th>Measured property</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>x</td>
</tr>
<tr>
<td>Aspect ratio distribution</td>
<td>x</td>
</tr>
<tr>
<td>XRD-profile and crystallinity index</td>
<td>x</td>
</tr>
</tbody>
</table>

4.4.1 Sampling

The wood powders produced with the air classifier mill and fluidised bed opposed jet mill as described in Papers I and II were sampled with a PT-type sample divider (Retsch, Germany) to obtain representative samples for analyses.

4.4.2 Analyses performed on diluted wood powder samples

Preparation of diluted wood powder samples

The diluted wood powder samples were prepared as described in Papers I–V.

Particle size distribution

The volumetric particle size distribution of diluted wood powder samples was measured with an LS 13320 laser diffraction-based particle size analyser.
(Beckmann Coulter, U.S.A). The median size, $d_{50}$, was used to represent the particle size and the dimensionless parameter $\Delta^*$ to represent the width of particle size distribution. The latter was calculated as

$$\Delta^* = \frac{d_{90} - d_{10}}{10 \mu m}, \quad (7)$$

where $d_{90}$ and $d_{10}$ are the particle sizes in micrometres corresponding to the 90% and 10% values in the cumulative size distribution, respectively. The size ratios $(d_{90}-d_{10})/d_{50}$ and $(d_{90}-d_{10})(2 \cdot d_{50})$ are more commonly used to provide information about the width of particle size distribution (Nakach et al. 2004, Adi et al. 2007, Palaniandy & Azizli 2009, Toraman 2011, Kotake et al. 2012) but these ratios depend on the median particle size of the product. To make comparison between samples with different median particle size easier the divider in the size ratios was replaced by a constant value of 10 μm.

**Aspect ratio distribution**

Aspect ratio distributions were measured from photos taken with a charged coupled device (CCD) as described in Papers I–V. The minimum aspect ratio (=1) represents a perfect filled circle. In the case of wood particles, a higher aspect ratio typically represents a more elongated shape. The cumulative aspect ratio distribution was used to calculate the median aspect ratio $AR_{50}$ and the width of the aspect ratio distribution $\Delta_{AR}$, the latter being defined as the difference between the aspect ratios corresponding to the 90% and 10% values in the distribution. An Ultra Plus field emission scanning electron microscope (Carl Zeiss, Germany) was used for the imaging of the finest particles to gain insight of their shape, but these images were not used to calculate the aspect ratio distribution.

### 4.4.3 Analyses performed on dry wood powder samples

**Preparation of the dry wood powder samples**

The wood powders produced as described in Papers I–II and V were used for the measurement of XRD profiles without drying, but all those produced for Paper IV were vacuum-dried before measuring the XRD profile.
**XRD profile and crystallinity index**

Tablets were prepared from the dry wood powders using a hydraulic press and X-ray diffraction profiles were measured with a D5000 diffractometer (Siemens, Germany) as described in Papers I, II, IV and V. The degree of crystallinity of the cellulose in terms of the crystallinity index (CrI) was calculated from the XRD profile in each case by the method proposed by Segal et al. (1959).

### 4.5 Modelling

Empirical models for specific energy consumption (SEC) and various wood powder properties were developed as a function of the operational parameters in Paper I. A Modde 7.0.0.1 software (Umetrics, Sweden) was used in the statistical analyses of the experimental data. In these statistical analyses, responses such as SEC and the various wood powder properties were modified with a mathematical operator to gain normally distributed data and good statistical significance for the models. The effects can be derived unambiguously from the coefficients of the empirical models and are therefore used as synonyms for them in the discussion. In Paper III the total available impact energy of the grinding ball in oscillatory ball milling was estimated (Eq. 3) and used to model the effects of the grinding ball mass, oscillation frequency and milling time on the properties of the wood powders and to estimate the specific energy consumption in fine grinding.
5 Results and discussion

5.1 Fine grinding of dried Norway spruce wood in impact mills

5.1.1 Air classifier mill

The SECs and the properties of the wood powders obtained from the air classifier mill are listed in Table 8, which indicates that the wood was ground to a median particle size of around 23 µm with a Δ* of over 5. The finest powders had AR$_{50}$ 2.3 and Δ$_{AR}$ 3.3 or higher (Table 8). To provide an insight into the shapes of the particles, CCD photos of sample ZPS 17 are presented in Fig. 11. The largest particles shown in Fig. 11a can be described as elongated and rectangular in shape rather than roundish, while the finest ones (Fig. 11c) resemble roundish particles but it is difficult to distinguish their shapes accurately because the pixel resolution of the CCD photos is around 1.6 µm. The FESEM image shown in Fig. 11d nevertheless suggests that they, too, are rectangular rather than roundish. The lowest CrI (approximately 41%) was obtained at the highest classifier and mill speeds, whereas reducing the mill speed from 20,000 min$^{-1}$ to 8000 min$^{-1}$ seemed to increase CrI. This means that air classifier milling had only a minor influence on the CrI of the wood by comparison with grinding media milling, where total amorphisation has proved possible (see Section 2.3.2). There were large variations in cellulose crystallinity between samples ground with similar processing parameters (see Table 8), possibly due to uneven drying conditions. Thermal treatment (Esteves & Pereira 2009), and also air-drying (Leppänen et al. 2011), may affect the cellulose crystallinity of wood. In this case drying was performed in large containers without any mixing, and therefore there were local variations in drying conditions depending on the position of the wood in the container.
Table 8. Specific energy consumption (SEC) in air classifier milling and the properties of the resulting wood powders. ‘Short’ and ‘long’ impact angles refers to the rotational direction of the rotor towards the short or long edge. Experiments ZPS10–ZPS18 are replicates for ZPS1–ZPS9. Modified from Paper I, published by permission of Elsevier.

<table>
<thead>
<tr>
<th>Experiment (run order)</th>
<th>Mill speed (min⁻¹)</th>
<th>Classifier speed (min⁻¹)</th>
<th>Impact angle</th>
<th>SEC (kWh t⁻¹)</th>
<th>(d_{50}) (µm)</th>
<th>(\Delta^*)</th>
<th>AR (_{50})</th>
<th>AR (_{\Delta})</th>
<th>Cr (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZPS1 (4)</td>
<td>8000</td>
<td>2000</td>
<td>Short</td>
<td>2505</td>
<td>208.5</td>
<td>76.8</td>
<td>2.8</td>
<td>6.3</td>
<td>47.2</td>
</tr>
<tr>
<td>ZPS2 (14) (^1)</td>
<td>8000</td>
<td>8000</td>
<td>Short</td>
<td>30,994</td>
<td>32.8</td>
<td>11.9</td>
<td>2.5</td>
<td>4.7</td>
<td>44.8</td>
</tr>
<tr>
<td>ZPS3 (11)</td>
<td>20,000</td>
<td>2000</td>
<td>Short</td>
<td>1712</td>
<td>223.0</td>
<td>70.7</td>
<td>3.5</td>
<td>6.6</td>
<td>49.6</td>
</tr>
<tr>
<td>ZPS4 (8) (^1)</td>
<td>20,000</td>
<td>8000</td>
<td>Short</td>
<td>4098</td>
<td>25.4</td>
<td>7.0</td>
<td>2.3</td>
<td>3.4</td>
<td>41.8</td>
</tr>
<tr>
<td>ZPS5 (5)</td>
<td>8000</td>
<td>2000</td>
<td>Long</td>
<td>2991</td>
<td>189.6</td>
<td>70.0</td>
<td>2.8</td>
<td>6.0</td>
<td>43.4</td>
</tr>
<tr>
<td>ZPS6 (3)</td>
<td>8000</td>
<td>8000</td>
<td>Long</td>
<td>38,160</td>
<td>33.0</td>
<td>12.1</td>
<td>2.5</td>
<td>4.7</td>
<td>45.9</td>
</tr>
<tr>
<td>ZPS7 (10)</td>
<td>20,000</td>
<td>2000</td>
<td>Long</td>
<td>1664</td>
<td>207.6</td>
<td>68.3</td>
<td>3.4</td>
<td>6.6</td>
<td>49.6</td>
</tr>
<tr>
<td>ZPS8 (1)</td>
<td>20,000</td>
<td>8000</td>
<td>Long</td>
<td>7879</td>
<td>25.9</td>
<td>7.5</td>
<td>2.4</td>
<td>3.7</td>
<td>41.2</td>
</tr>
<tr>
<td>ZPS9 (6)</td>
<td>14,000</td>
<td>5000</td>
<td>Short</td>
<td>2593</td>
<td>49.1</td>
<td>15.8</td>
<td>2.8</td>
<td>5.2</td>
<td>43.0</td>
</tr>
<tr>
<td>ZPS10 (2)</td>
<td>8000</td>
<td>2000</td>
<td>Short</td>
<td>2549</td>
<td>198.4</td>
<td>71.7</td>
<td>2.8</td>
<td>6.3</td>
<td>49.3</td>
</tr>
<tr>
<td>ZPS11 (15)</td>
<td>8000</td>
<td>8000</td>
<td>Short</td>
<td>17,589</td>
<td>32.7</td>
<td>12.3</td>
<td>2.4</td>
<td>4.8</td>
<td>45.5</td>
</tr>
<tr>
<td>ZPS12 (9)</td>
<td>20,000</td>
<td>2000</td>
<td>Short</td>
<td>1723</td>
<td>249.5</td>
<td>80.0</td>
<td>3.5</td>
<td>6.6</td>
<td>50.2</td>
</tr>
<tr>
<td>ZPS13 (13) (^1)</td>
<td>20,000</td>
<td>8000</td>
<td>Short</td>
<td>6648</td>
<td>23.0</td>
<td>5.6</td>
<td>2.3</td>
<td>3.3</td>
<td>41.5</td>
</tr>
<tr>
<td>ZPS14 (18)</td>
<td>8000</td>
<td>2000</td>
<td>Long</td>
<td>2431</td>
<td>189.9</td>
<td>69.6</td>
<td>2.7</td>
<td>5.9</td>
<td>48.2</td>
</tr>
<tr>
<td>ZPS15 (17)</td>
<td>8000</td>
<td>8000</td>
<td>Long</td>
<td>17,496</td>
<td>31.6</td>
<td>11.8</td>
<td>2.4</td>
<td>4.6</td>
<td>46.3</td>
</tr>
<tr>
<td>ZPS16 (7)</td>
<td>20,000</td>
<td>2000</td>
<td>Long</td>
<td>1844</td>
<td>232.9</td>
<td>72.8</td>
<td>3.5</td>
<td>6.8</td>
<td>48.0</td>
</tr>
<tr>
<td>ZPS17 (16)</td>
<td>20,000</td>
<td>8000</td>
<td>Long</td>
<td>4310</td>
<td>23.8</td>
<td>6.2</td>
<td>2.3</td>
<td>3.4</td>
<td>44.5</td>
</tr>
<tr>
<td>ZPS18 (12)</td>
<td>14,000</td>
<td>5000</td>
<td>Short</td>
<td>2588</td>
<td>44.6</td>
<td>14.5</td>
<td>2.7</td>
<td>4.8</td>
<td>45.7</td>
</tr>
<tr>
<td>ZPS19 (19)</td>
<td>20,000</td>
<td>8000</td>
<td>Long</td>
<td>4245</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^1\) Grinding time was less than 40 min
Development of wood powder properties

The results of experiments ZPS1–ZPS18 (Table 8) were used for modelling of the wood powder properties as a function of the processing parameters. The coefficients used in these empirical models for the wood powder properties are shown in Fig. 12 and the main statistical parameters for the models in Table 9. The high values for $R^2$, $R^2(\text{Adj.})$, $Q^2$ and reproducibility in Table 9 indicate that the empirical models are statistically valid and the results reproducible, except in the case of the crystallinity index. The model validity is over 0.25 for all the properties studied (see Table 9) and therefore there is no lack of fit in the models. In the case of $\Delta_{MB}$ the low model validity can be considered an artefact, since the other statistical parameters are well over 0.9 (see Table 9). The reason for poor statistical values in empirical model for CrI was the large variations in CrI values,
even when similar processing parameters were used (Table 8). The reason for the poor statistical values in the empirical model for CrI lay in the large variations in CrI values even when similar processing parameters were used (Table 8). According to Fig. 12, the classifier speed, mill speed and their interaction had a significant influence on the wood powder properties, but the choice between long and short edges had a negligible influence, because the respective coefficients with error bars cross the zero line (Fig. 12). The classifier speed alone had the most significant effect on the properties of the wood powders (Fig. 12). Contour plots for the empirical models for wood powder properties as a function of mill and classifier speeds in the speed ranges studied here are shown in Fig. 13. The effect of the impact angle is ignored in the models due its insignificant influence on the properties of the wood. Fig. 13 suggests that there is a certain classifier speed for every wood powder property at which changes in mill speed do not influence the property and above which the influence of mill speed is the reverse of what it was below that speed.

![Fig. 12. Scaled and centred coefficients in the empirical models for the development of wood powder properties in air classifier milling. The empirical models depict responses that have been modified with the mathematical operator mentioned on the y-axis. Modified from Paper I, published by permission of Elsevier.](image)
Table 9. Main statistical parameters of the empirical models for the wood powder properties (95% confidence level and normal distribution). Modified from Paper I, published by permission of Elsevier.

<table>
<thead>
<tr>
<th>Property</th>
<th>$R^2$</th>
<th>$R^2$ (Adj.)</th>
<th>$Q^2$</th>
<th>Model validity</th>
<th>Reproducibility</th>
<th>Cond. no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{50}$</td>
<td>0.998</td>
<td>0.997</td>
<td>0.995</td>
<td>0.857</td>
<td>0.997</td>
<td>6.214</td>
</tr>
<tr>
<td>$\Delta^*$</td>
<td>0.996</td>
<td>0.994</td>
<td>0.991</td>
<td>0.853</td>
<td>0.994</td>
<td>6.214</td>
</tr>
<tr>
<td>AR$50$</td>
<td>0.986</td>
<td>0.982</td>
<td>0.976</td>
<td>0.912</td>
<td>0.979</td>
<td>1.118</td>
</tr>
<tr>
<td>$\Delta_{AR}$</td>
<td>0.985</td>
<td>0.980</td>
<td>0.973</td>
<td>0.442</td>
<td>0.987</td>
<td>1.118</td>
</tr>
<tr>
<td>CrI</td>
<td>0.728</td>
<td>0.644</td>
<td>0.480</td>
<td>0.750</td>
<td>0.666</td>
<td>1.118</td>
</tr>
</tbody>
</table>

Fig. 13. Contour-plotted empirical models for given wood powder properties as a function of the classifier and mill speeds. The effect of the impact angle is ignored. Modified from Paper I, published by permission of Elsevier.

Specific energy consumption

An SEC of over 5.8 kJ g$^{-1}$ (1600 kWh t$^{-1}$) was needed to obtain a $d_{50}$ of around 190 µm in the fine grinding of Norway spruce wood, and over 15.5 kJ g$^{-1}$ (4300 kWh t$^{-1}$) to obtain a $d_{50}$ of around 23 µm (Table 8). When a low mill speed was used with the highest classifier speed, $d_{50}$ was approximately 10 µm higher and the specific energy consumption more than doubled relative to processing at a high mill speed (Table 8). The increased specific energy consumption indicates that a mill speed of 8000 min$^{-1}$ provides insufficient stress energy when grinding.
wood to a median particle size range of around 30 µm, so that higher mill speeds should be used for fine grinding purposes.

The results shown in Table 8 were used for modelling SEC as a function of the processing parameters. The specific energy consumption figures obtained in experiments ZPS2, ZPS4, ZPS8 and ZPS13 were not included in the modelling because the grinding time was less than 40 minutes, which will have had a significant influence on the SEC (see Paper I for details). The coefficients in the empirical model for the specific energy consumption in which the response is the inverse value of SEC are shown in Fig. 14, as also are the main statistical parameters of the empirical model. The high values for $R^2$, $R^2(\text{Adj.})$, $Q^2$ and reproducibility in Fig. 14 indicate that the model is statistically valid and the results are reproducible. Since the validity of the model is above 0.25, the error in the model is in the same range as pure error. Fig. 14 also shows that the classifier speed and mill speed had an influence on the average specific energy consumption in fine grinding, the classifier speed being the most significant single factor (Fig. 14). The use of a higher classifier speed led to a higher specific energy consumption, because the classifier wheel needed more power from the motor to revolve faster. Another reason is that as the classifier speed increases the particles need to be finer to get past the classifier and therefore their residence time in the grinding and classifying section increases. This reduces the production rate and increases the energy demand of the rotor in the grinding zone. The specific energy consumption in air classifier milling can be reduced by using a higher rotor speed (Figs. 14 and 15). The choice between the long and short impact edge had a negligible effect, since their coefficients with error bars cross the zero line (Fig. 14). A contour plot of the modelled specific energy consumption as a function of the classifier and mill speeds in the speed ranges studied here is shown in Fig. 15. Since the start-up of the process is inefficient in terms of energy and the feeding speed was not optimised, the specific energy consumption can be expected to be lower in an industrial process that is continuous and well optimised.
5.1.2 Fluidised bed opposed jet mill

As seen in Fig. 16, dried Norway spruce wood was ground in an opposed jet mill to a median particle size of around 18 µm, giving a $\Delta^*$ of around 5. The finest powders produced had $\text{AR}_{50}$ 2.5 and $\Delta_{\text{AR}}$ 3.6 or higher. The aspect ratios were slightly higher than those for the finest powders produced with the air classifier mill (see Table 8 and Fig. 16), and therefore the jet milled particles are smaller and more elongated. This difference may, however, be due to the removal of
finest particles after pregrinding rather than to the different milling technique. To provide an insight into the shapes of the particles, CCD photos of particles in jet milled sample AFG-P8, with a median particle size of around 20 µm, are shown in Fig. 17 (see Paper II for detailed information on the sample). The largest and intermediate-sized wood particles, shown in Fig. 17a, can be described as elongated, while the finest particles resemble roundish ones, as in air classifier sample ZPS 17 (Figs 11c and 17c). When a grinding pressure of 10 bar was applied at a classifier speed of 20,000 min⁻¹ CrI was reduced from 47.5% to around 44%, which means that opposed jet milling had only a minor influence on CrI.

Fig. 16. Development of (a) $d_{50}$, (b) $\Delta^*$, (c) AR$_{50}$, (d) $\Delta_{AR}$ and (e) CrI as a function of classifier speed in opposed jet milling. Low GP stands for the grinding pressure approximately 6 bar and High GP stands for the grinding pressure approximately 10 bar.
Fig. 17. Three CCD photos showing some of the a) largest b) intermediate-sized, c) finest observable wood particles, and d) FESEM image showing some small rectangular-shaped particles in opposed jet milled sample AFG-P8.

Development of wood powder properties

According to Fig. 16 the grinding pressure had substantial influence on particle size and shape when the classifier speed was around 8000 min\(^{-1}\). This effect may be due to the higher air flow rate in the case of a higher grinding pressure (see Table 10), thus causing larger particles to pass through the classifier than with a lower flow rate at a similar classifier speed. The air flow exerts a drag force on the particles, driving them past the classifier wheel and into the product container (see Benz et al. 1996). This drag force will depend on the particle size, with a higher air flow rate increasing the particle size of the product. The increase in aspect ratio is probably connected with the increased particle size. The influence of the air flow rate on the particle properties became negligible at a classifier speed of 20,000 min\(^{-1}\) (Fig. 16), even though a significant decrease in cellulose crystallinity still took place at this classifier speed when a high grinding pressure
was used (Fig. 16). This means that a grinding pressure of approximately 10 bar (overpressure) was enough to cause reduced cellulose crystallinity when $d_{50}$ was less than 70 µm (Fig. 16), whereas the use of a low grinding pressure caused a very small or negligible decrease in CrI even though the wood was ground down to a median particle size of 20 µm (Fig. 16).

Table 10. Averaged processing parameters, specific energy consumption and product information on the jet milling experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Classifier</th>
<th>Grinding air</th>
<th>Total air</th>
<th>Feed or Product</th>
<th>Energy</th>
<th>SEC x10^-3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Speed (min^-1)</td>
<td>Pressure1 (bar)</td>
<td>Volume (Nm³)</td>
<td>Compression work^2 (MJ)</td>
<td>Flow rate (Nm³ h^-1)</td>
<td>Dry mass m_P,dry (g)</td>
</tr>
<tr>
<td>FEED</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>199 ± 6</td>
</tr>
<tr>
<td>AFG-P1</td>
<td>8040</td>
<td>5.92</td>
<td>7.23</td>
<td>1.42</td>
<td>86.18</td>
<td>25.92</td>
</tr>
<tr>
<td>AFG-P2</td>
<td>20.010</td>
<td>5.93</td>
<td>7.00</td>
<td>1.37</td>
<td>85.65</td>
<td>13.34</td>
</tr>
<tr>
<td>AFG-P3</td>
<td>8040</td>
<td>9.89</td>
<td>11.63</td>
<td>2.81</td>
<td>96.64</td>
<td>59.02</td>
</tr>
<tr>
<td>AFG-P4</td>
<td>19.980</td>
<td>9.68</td>
<td>11.38</td>
<td>2.75</td>
<td>94.70</td>
<td>29.71</td>
</tr>
<tr>
<td>AFG-P5</td>
<td>8010</td>
<td>5.93</td>
<td>7.20</td>
<td>1.41</td>
<td>86.37</td>
<td>40.05</td>
</tr>
<tr>
<td>AFG-P6</td>
<td>20.010</td>
<td>5.93</td>
<td>6.99</td>
<td>1.37</td>
<td>85.50</td>
<td>12.82</td>
</tr>
<tr>
<td>AFG-P7</td>
<td>8040</td>
<td>9.89</td>
<td>11.58</td>
<td>2.80</td>
<td>96.34</td>
<td>59.97</td>
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<tr>
<td>AFG-P8</td>
<td>20.010</td>
<td>9.83</td>
<td>11.87</td>
<td>2.87</td>
<td>95.98</td>
<td>32.34</td>
</tr>
</tbody>
</table>

^1 Excess pressure compared with normal air pressure (NTP). ^2 Compression work calculated using Equation 2 with $M_r = 28.96$ g mol^-1, $PUC = 101,325$ Pa, $\rho = 1204$ g m^-3, $T = 293.15$ K and the averaged pressure of the grinding air. ^3 Measured in wood powder collected from the container after the classifier, thus not including particles conducted to the filtering stage.

Specific energy consumption

Since most of the energy needed for processing in a jet mill is consumed in compressing the pressurised air, it was the work needed for this purpose that was considered here. The averaged processing parameters for the fine grinding of dried Norway spruce wood in a fluidised bed opposed jet mill are listed in Table 10. Only dry air was considered when calculating the compression work. An increase in classifier speed reduced the median particle size and the dry mass of the product (Table 10), while an increase in grinding pressure increased the median size and mass of the product, i.e. the production rate (Table 10). A small decrease in the total average flow rate of air was observed on every occasion when a higher classifier speed was used rather than a lower one, given that the grinding pressure was kept constant (Table 10). On the other hand, when the
classifier speed was kept constant the total average flow rate of air, the volume of the grinding air and the work needed for compressing the grinding air increased on every occasion when the grinding pressure was increased (Table 10). The specific energy consumption in milling was mainly affected by the classifier speed (Table 10). At high classifier speeds the use of a higher grinding pressure reduced the specific energy consumption but increased the median particle size of the product (Table 10). As seen in Table 10, over 32 kJ g⁻¹ (approx. 9 MWh t⁻¹) but less than 55 kJ g⁻¹ (approx. 15 MWh t⁻¹) was needed to obtain wood powders with a median particle size between 48.2 µm and 69.2 µm from a feed with \( d_{50} = 199 \mu m \) (± 6 µm), and over 88 kJ g⁻¹ (approx. 25 MWh t⁻¹) to obtain a median particle size of around 20 µm (Table 10). Although the compression work considers the ideal minimum work needed for compression, the fine grinding was not fully optimised because the feeding rate was kept constant. The experiments also involved an energy inefficient start-up period. Thus the energy consumption may be even lower in an optimised continuous process.

5.1.3 Oscillatory ball mill

Dried Norway spruce wood was ground to a median particle size of less than 18 µm with a \( \Delta^* \) of around 5 with the oscillatory ball mill, and the finest powders produced had \( AR_{50} \) and \( \Delta_{AR} \) significantly lower than 2.0 (Fig. 18). These values are much lower than for the finest powders produced with the air classifier mill or the opposed jet mill (see Table 8 and Fig. 16), and therefore oscillatory ball milling can be said to produce particles that are smaller and rounder than in either of the above. To provide an insight into the shapes of the particles, CCD photos of the powder produced in the oscillatory ball mill, with a median particle size of around 20 µm, are presented in Fig. 19. All of the wood particles shown in this figure can be described as rectangular or roundish. FESEM images of some of the finest particles obtained by this method are shown in Fig. 20. It was also possible to produce wood powders by oscillatory ball milling that had a median particle size over 100 µm with an \( AR_{50} \) of less than 1.8 and a \( \Delta_{AR} \) less than 2.4 (Fig. 18).
Fig. 18. Effect of grinding ball mass and oscillation frequency on the a) $d_{50}$, b) $\Delta^*$, c) AR50, d) $\Delta_{AR}$ and e) temperature change as a function of the total available impact energy of the grinding ball, $E_T$. The mass of the feed in each setup was 1 g. Data points containing an open space indicate the large end cut in the particle size distribution. Modified from Paper III, published by permission of Elsevier.
Fig. 19. Three CCD photos showing some of the a) largest, b) intermediate-sized and c) finest observable wood particles in an oscillatory ball milled sample with $d_{50} = 21.5$ μm, $\Delta^* = 5.8$, $AR_{50} = 1.6$ and $\Delta_{AR} = 1.5$.  

Fig. 20. Eight different FESEM images a)-h) taken from one oscillatory ball milled wood powder sample. Modified from Paper II, published by permission of Elsevier.
Development of wood powder properties

According to Fig. 18, the total kinetic energy of the grinding ball $E_T$ (see Paper III) predicts the development in the size and shape properties of dried Norway spruce wood in oscillatory ball milling upon a change in the mass of the grinding ball or its oscillation frequency. It is therefore proposed that the mathematical model evaluated here (Eq. 3) can be applied as a simplified mill based stressing model to oscillatory ball milling in impact mode (for further information about the impact mode, see Chen Y et al. 2004) for predicting milling behaviour when changing the oscillation frequency, mass of the grinding ball (but not its volume) and milling time. In this model the stressing energy is $E_s$ (Eq. 4), the stress number is $S_{N_e}$ (Eq. 5) and stressing type is double impact (see Section 2.2.2). The median particle size was inversely linearly dependent on $E_T$ in the $E_T$ range considered before achieving a median particle size of 20 µm (Fig. 18a). The mathematical model plotted in Fig. 18a is the same as Rittinger’s model, which is commonly used in mineral processing to model the energy consumption when considering particle sizes in the range 10–1000 µm (Lowrison 1974: 54–55). Rittinger’s model has also been found to apply to the fine grinding behaviour of $\alpha$-lactose monohydrate in oscillatory ball milling in impact mode (Chen Y et al. 2004). When processing was continued after a median particle size of 20 µm had been obtained, which occurred at $E_T = 1360$ J according to the model derived here, the resistance of the wood to further size reduction increased considerably and its particle size properties ($d_{50}$ and $\Delta^*$) flattened out at a certain level or even increased (Figs. 18a and b). The smallest median particle size was found to be between 13 µm and 20 µm for all the studied setups (Fig. 18a). In the case of setups B–D the temperature change increased significantly when the particle size properties evened out at a certain level (Figs. 18a, b and e). The rise in temperature and sudden increase in comminution resistance indicate the presence of viscoelastic behaviour in wood. This viscoelasticity is most likely the main reason why the size properties of Norway spruce wood evened out at a certain particle size range even though higher impact energies were used in processing and pulverisation was continued after the minimum size had been attained. On the other hand, $AR_{50}$ and $\Delta AR$ did not flatten out at the same point as the median particle size as a function of $E_T$ (Fig. 18a–d). This means that the particles do not break due to fragmentation, because their volume-based particle size properties remained unchanged. Presumably there may be a surface breakage mechanism, attrition, involved. Attrition causes particles to become rounder but has an
insignificant effect on their volume-based size properties. In addition, the changes in aspect ratio may be also due to deformation of the wood particles under repeated stress that together with temperature change suggests viscoplastic behaviour of Norway spruce wood once the minimum particle size has been reached (Fig. 18). This observation suggests the presence of globular-shaped particles that tend to agglomerate with prolonged milling times, as first described for Norway spruce wood by Maurer and Fengel (1992). FESEM images of particles found in an oscillatory ball milled sample are shown in Fig. 20, where the roundish particles in Figs. 20g and h could be the globular shaped particles that tend to agglomerate. Fig. 21 shows how varying the mass of the feed (setups D–G) can affect the development of inverse values for $d_{50}$ and $\Delta^*$ as a function of $E_T$. According to Fig. 21a, median size follows an inverse linear trend as a function of $E_T$ (Rittinger’s model) in the particle size range between 20 µm and 100 µm when the mass of the feed is between 1 g and 3 g. In the case of setup E the trend is non-linear (Fig. 21a) and therefore cannot be modelled with Rittinger’s model.
Fig. 21. Effect of changes in the amount of feed on the inverse of a) median size and b) width of the particle size distribution as a function of total available impact energy of the grinding ball, $E_T$. The black line represents the model for setups B–D introduced in Fig. 18. Data points containing an open space indicate the large end cut in the particle size distribution. Modified from Paper III, published by permission of Elsevier.

**Specific energy consumption**

The specific energy consumption for different amounts of feed is shown in Fig. 22. Setup E is the least energy efficient when the desired median particle size is less than 100 µm. The reason for the different comminution behaviour in the case of setup E is probably the low amount of feed, which makes it possible for some collisions to occur between the grinding ball and the grinding jar with little or no wood present in the impact zone. According to Fig. 22, dried and screened Norway spruce sawdust can be pulverised down to $d_{50} = 100$ µm with a minimum specific energy consumption of 0.36 kJ g$^{-1}$ (100 kWh t$^{-1}$) and down to $d_{50} = 20$ µm with 1.4 kJ g$^{-1}$ (380 kWh t$^{-1}$) when considering the total available impact energy of the grinding ball in fine grinding. Kobayashi et al. (2008) has reported that 800
kWh t⁻¹ was consumed for the whole process when Norway spruce wood chips were pulverised from 22 mm down to 150 µm with a vibration mill. The specific energy consumption calculated from the estimated total available impact energy of the grinding ball (SECOSC) considers only the energy available for particle size reduction, which is lower than the total electrical energy consumed by the equipment, due to energy losses in driving the mill and in the electronics. On the other hand, the theoretical energy needed for the generation of new surfaces can be considered to be lower than the estimated SECOSC. Only in the ideal case, where the total available impact energy in the process is applied for the generation of new surfaces, should the estimated SECOSC be the same as the theoretical energy needed for the generation of the new surface area. Since this ideal situation will never exist in practical comminution, the estimated SECOSC will always be higher than the theoretical energy needed for the generation of new surfaces. Therefore the estimated SECOSC provides a better practical value for the energy consumption than can be gained by calculating the theoretical energy for the generation of new surfaces and can be regarded as a good target for the optimisation of impact-based mills involving grinding media.

Fig. 22. Effect of the feed amount of feed on median particle size as a function of the specific energy consumption. The data point containing an open space indicates a large end cut in the size distribution. Modified from Paper III, published by permission of Elsevier.
5.2 Comparison of impact milling techniques

Influence of double impacts on the development of wood properties in milling

Figs. 23–25 show the development of $\Delta^*$, AR$_{50}$, $\Delta_{AR}$ and CrI in opposed jet milling and oscillatory ball milling as a function of median particle size. In oscillatory ball milling $\Delta^*$ followed a linear trend as a function of $d_{50}$ in fine grinding from a $d_{50}$ of 199 µm ($\pm$ 6 µm) down to around 20 µm (Fig. 23), while in the case of the jet milled samples $\Delta^*$ decreased as a function of $d_{50}$ and was approximately identical to the particle size distribution of the oscillatory ball milled samples when considering a median particle size around 20 µm (Fig. 23). Median aspect ratio and $\Delta_{AR}$ decreased more as a function of $d_{50}$ in oscillatory ball milling than in opposed jet milling (Fig. 24). The CCD photos shown in Fig. 26 provide an insight into the differences between the milling techniques in terms of the aspect ratio distribution when $d_{50}$ is around 20 µm. Opposed jet milling had a significantly lower effect on the crystallinity index than did oscillatory ball milling when the wood was ground down to a $d_{50}$ around 20 µm (Fig. 25).

Fig. 23. Effect of oscillatory ball milling and opposed jet milling on the development of the width of the particle size distribution $\Delta^*$ as a function of the median particle size $d_{50}$. High GP and low GP mean average excess pressures of the grinding air of approximately 10 bar and 6 bar, respectively. Paper II, published by permission of Elsevier.
Fig. 24. Effect of oscillatory ball milling and opposed jet milling on the development of a) the median aspect ratio $AR_{50}$ and b) the width of the aspect ratio distribution $\Delta AR$ as a function of the median particle size $d_{50}$. High GP and low GP are as in Fig. 23. Modified from Paper II, published by permission of Elsevier.

Fig. 25. Effect of the milling technique on development of the crystallinity index CrI as a function of the median particle size $d_{50}$. High GP and low GP are as in Fig. 23. Paper II, published by permission of Elsevier.
Fig. 26. CCD photos showing some of the largest wood particles from a) the feed, b) the product of opposed jet milling and c) the product of oscillatory ball milling. The jet milled and oscillatory ball milled particles were of a median size of around 20 µm. Modified from Paper II, published by permission of Elsevier.

The feed used in the jet milling and oscillatory ball milling experiments was produced from a similarly treated raw material to that used in the air classifier milling experiments. Also the feed was preground with the same air classifier mill as was used in the air classifier milling experiments, but the finest particles were removed from the feed prior to jet and oscillatory ball milling. Although a $d_{50}$ of around 23 µm was obtained in air classifier milling, CrI (%) could not be reduced below 41% and the minimum $AR_{50}$ and $\Delta AR$ were 2.3 and 3.3, respectively (Table 8). Thus the greatest differences in the properties of the wood powders were observed between the media and non-media impact mill experiments (Figs. 23–25 and Table 8). In fine grinding of dried Norway spruce wood the presence of double impacts favoured the production of rounder shaped particles with low cellulose crystallinity by comparison with single impacts (Figs. 23–25 and Table 8).

**Specific energy consumption**

When comparing specific energy consumption it is important first to consider the desired properties of the wood powder. When high cellulose crystallinity and aspect ratio are required in dried Norway spruce the suitable impact-based fine grinding techniques would be opposed jet mills and rotor impact mills. In the present experiments it was possible to reduce Norway spruce wood from a median particle size between 1 mm and 2 mm down to 23.8 µm with a specific energy consumption of 15.5 kJ g$^{-1}$ by air classifier milling (Table 8), whereas opposed jet milling consumed over 32 kJ g$^{-1}$ in producing wood powder with a median particle size of 48.2 µm from a significantly smaller feed than that was
used in air classifier milling (Table 10). It should therefore be suggested that an air classifier mill is more energy efficient technique than a fluidised bed opposed jet mill for pulverising dried Norway spruce wood. In fact, the electric power demand in the case of air classifier milling can be even lower in an industrial-scale production plant. In the case of jet milling, the milling chamber in the laboratory model has been built by Hosokawa Alpine with a similar architecture to that of the larger-scale equipment of the AFG product family, so that the use of compression energy for particle breakage in the laboratory equipment can be considered to be very close to that observed in an industrial-scale milling plant with a similar jet mill. It might be possible to optimise both types even further by increasing the feed rate.

The specific energy consumption in the impact milling of dried Norway spruce wood with a median particle size between 1 mm to 2 mm with media mills can be as low as 0.36 kJ g\(^{-1}\) for a targeted \(d_{50}\) of 100 µm and 1.40 kJ g\(^{-1}\) for a \(d_{50}\) of 20 µm (Fig. 22). This specific energy consumption does not consider the energy losses in driving the machine or any additional equipment, which are naturally included in the specific energy consumption when considering the electric energy demand of the mill. It therefore seems possible to obtain a lower energy consumption with media mills than with an air classifier mill, but this depends on the consumption of energy that is not directed at the comminution of particles. This energy is significantly affected by the architecture of a media mill. Kobayashi et al. (2012), studying the significance of the architecture of vibration mills for energy efficient wood powder production, concluded that a multiple tube vibration mill is more energy efficient than a single tube vibration mill and estimated the specific energy consumption in the fine grinding of wood to be 1.0 kJ g\(^{-1}\) when using a multiple tube vibration mill. This figure is very close to the values obtained in the present oscillatory ball milling experiments (Fig. 22), so that media milling appears to be well suited for wood pulverisation.
5.3 Effects of pretreatments and milling conditions on the properties of Norway spruce wood in impact-based media milling

5.3.1 Drying and cryogenic grinding conditions

Development of $d_{50}$, $\Delta^*$, $AR_{50}$ and $\Delta AR$ under ambient and cryogenic grinding conditions is shown as a function of moisture content in Fig. 27, which suggests that while moisture content has a significant influence on wood powder properties under ambient grinding conditions, these properties are less dependent on moisture content under cryogenic conditions (Fig. 27). When comparing grinding conditions given the same moisture content (Fig 27a), it can be seen that a smaller median particle size was obtainable under cryogenic conditions. When considering the moisture contents of 1%, 27% and 50% in Fig 27a, increasing the grinding time from 10 min to 30 min under ambient conditions did not reduce the median particle size any further than had been obtained by cryogenic grinding for 10 min. It therefore seems that the use of cryogenic grinding conditions rather than ambient conditions provides better energy efficiency in the fine grinding of Norway spruce wood. Wood powder with a median particle size of less than 13 µm was obtained only under cryogenic conditions (Fig. 27a), when the finest wood powder had a median size of 7.4, $\Delta^* = 2.04$, $AR_{50} = 1.67$ and $\Delta AR = 1.78$. It has not been possible to produce wood powders with a median particle size significantly less than 13 µm in any other way (Figs 18, 27 and Tables 8 and 10). It was possible to produce fine powders with a median particle size below 100 µm an elongated particle shape ($AR_{50} \approx 3.0$ and $\Delta AR \approx 6.0$) under ambient conditions by pulverising Norway spruce wood with a moisture content of 44% (Fig. 27). The CCD photos and FESEM images of various wood powders in Figs. 28 and 29 illustrate the differences in particle shape between the powders with different $AR_{50}$ and $\Delta AR$ values obtained by oscillatory ball milling. Vibration mills are generally regarded in the literature as representing a technique for producing roundish particles from wood (see Section 2.3.2), but milling moist wood under ambient conditions does in effect produce elongated particles with $AR_{50}$ and $\Delta AR$ values very close to those produced with a rotor impact mill and jet mill (Figs. 24, 25, 27 and Table 8). The reason suggested for this is softening of the hemicelluloses due to the plasticising effect of water at room temperature, which favours cleavage in the primary and secondary cell wall layers (Jääskeläinen & Sundqvist 2007: 127–130). Under cryogenic grinding conditions the temperature
is too low for any softening of the hemicelluloses and thus the particle shapes are similar to those obtained from dried wood. In fact, the oscillatory ball milling experiments with dried Norway spruce wood yielded some particles with a scaly surface (see Figs. 20h and g), as were also found when wood powders were milled under cryogenic conditions (Fig. 30).

Fig. 27. The differences between ambient and cryogenic grinding conditions in a) \(d_{50}\), b) \(\Delta^*\), c) \(AR_{50}\) and d) \(\Delta AR\) as a function of moisture content in oscillatory ball milling. The black data points represent experiments with replicates and the empty data points indicate a large-end cut in the particle size distribution. Modified from Paper IV, published by permission of De Gruyter.
Fig. 28. CCD photos from three wood powder samples with different aspect ratio properties. In the figure there is shown three photos from each sample to illustrate differences in different particle size ranges. Paper IV, published by permission of De Gruyter.

Fig. 29. FESEM images of two wood powder samples. Paper IV, published by permission of De Gruyter.

Fig. 30. FESEM images of a wood powder sample milled under cryogenic conditions.
The crystallinity indices of oscillatory ball milled samples pulverised under ambient and cryogenic conditions for different periods of time are listed in Table 11. Segal et al. (1959) developed the method for estimating the relative degree of cellulose crystallinity in cotton celluloses and therefore one explanation for the negative CrI values shown in Table 11 can be due the differences in the X-ray diffraction patterns between cotton cellulose and Norway spruce wood. The CrI of the fresh feed was 39% and that of the oven-dried feed was also 39%, so there were no observable changes in CrI due to oven-drying of the wood. It may be seen from Table 11 that oscillatory ball milling of Norway spruce wood for at least 10 min lowered the CrI by at least 4%-units. The fine grinding of wood a with moisture content over 27%, which is slightly above the fibre saturation point of Norway spruce wood (see Section 2.1.2), under ambient conditions had little effect on CrI (Table 11), but when considering the milling of feeds with moisture contents between 1% and 27% under ambient conditions, a lower CrI was obtained with the samples that had a lower initial moisture content when milling for 10 min (Table 11). In the case of the feed with a moisture content of 1%, a longer grinding time reduced the CrI even more (Table 11), but when wood with a moisture content between 8% and 50% was milled for 10 min under cryogenic conditions the crystallinity indices varied between 24% and 30% (Table 11). When samples with an initial moisture content of 1% were milled under cryogenic conditions for 10 min the CrI was significantly lower than in the other samples milled under similar conditions (Table 11). Under cryogenic conditions a longer grinding time reduced CrI when the moisture content was between 1% and 50% (Table 11). Thus cryogenic grinding offers a good way of reducing the cellulose crystallinity of wood with a moisture content well above the fibre saturation point, which seems not to be possible under ambient conditions. Consequently, it seems that the presence of bound, and more especially unbound, water in Norway spruce wood plays a crucial role in protecting the crystalline cellulose from destruction when exposed to double impacts. This protective capability seems to be lost when the water is in a solid state during milling.
Table 11. Crystallinity indices of oscillatory ball milled wood samples. Modified from Paper IV, published by permission of De Gruyter.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Milling time (min)</th>
<th>CrI (%) when the moisture content of the feed was</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50% 27% 17% 8% 1%</td>
</tr>
<tr>
<td>Ambient</td>
<td>0</td>
<td>39    39</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>35    32 20 10 -5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>34    33 30 -9</td>
</tr>
<tr>
<td>Cryogenic</td>
<td>10</td>
<td>24    21 30 26 10</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>10    -1 -9</td>
</tr>
</tbody>
</table>

*Milling time of 0 min refers to the feed*

Fine grinding of moist Norway spruce wood was also tested with a high-speed rotor impact mill and a fluidised bed opposed jet mill, but it was found that the wood agglomerated in front of the feeding screw until it totally obstructed the feed. Agglomeration was also observed in oscillatory ball milling, where the samples of wood with a moisture content above 44% formed pancake-shaped agglomerations at the end wall of the grinding chamber during milling. It was possible to disperse these agglomerates, however, when preparing diluted samples for the analyses, but this had to be helped along mechanically with a glass stick prior to agitation with a magnetic stirrer. Agglomeration of moist wood in dry grinding have also been reported by Gravelsins (1998) in Szego milling experiments, where it was observed that moist wood particles of size below 150 µm agglomerated to form larger particles.

5.3.2 Mild torrefaction

The correlations between $\Delta^*$ and $d_{50}$ for dried and torrefied samples ground for different periods of time are shown in Fig. 31. Mild torrefaction had an insignificant influence on $\Delta^*$ as a function of $d_{50}$, and when the mass loss ($M_L$) was less than 0.2% it had no influence on $d_{50}$ as a function of $E_T$. Torrefaction involving an $M_L$ over 1.4%, however, reduced the $E_T$ needed for obtaining a given median particle size over 17.4 µm (± 0.2 µm) (Fig. 32). Specific energy consumptions for the setups REF, TOR B and TOR C are listed in Table 12, which indicates that a smaller median particle size was obtained with a similar SECOSC when torrefaction pretreatment was more intensive and the median particle size was over 17.4 µm. In the TOR C experiments where $d_{50}$ was similar or smaller than in the REF experiments the specific energy consumption decreased by approximately 21–33% following TOR C pretreatment when the
targeted $d_{50}$ was between 18.7 µm ($\pm$ 0.5 µm) and 79 µm ($\pm$ 3 µm) (Table 12), but once $E_T = 3422$ J was reached the differences in $d_{50}$ between the REF, TOR B and TOR C experiments became insignificant. When $E_T$ increased above 3422 J no significant decreases in $d_{50}$ were observed (Fig. 32). There is therefore a certain particle size range in which torrefaction pretreatment cannot improve the energy efficiency, and this coincides with the smallest particle size range obtained with dried samples, i.e. 13–20 µm (see Section 5.1.3). Also the minimum median particle size obtained with torrefied samples, 12.9 µm ($\pm$ 0.6 µm) (Table 12), is not significantly lower than the minimum median particle size of 13 µm reported in Section 5.1.3. The reason for this is thought to be agglomeration of the globular shaped particles and increased viscoelasticity of the wood when milling down to $d_{50}$ values below 20 µm, as reported and discussed in Section 5.1.3. Mild torrefaction did not influence the median aspect ratio when $E_T$ was over 1000 J (Fig. 33a), but when it was below 1000 J the differences in AR$_{50}$ between the REF and torrefied samples were fairly small (Fig. 33a). According to Fig. 33b, the differences between the REF and torrefied samples were insignificant when considering $\Delta_{AR}$ as a function of $d_{50}$. Mild torrefaction with an $M_l$ up to 2.8% had a negligible effect on CrI when considering between REF and TOR C results obtained with similar $E_T$ values or milling times (Table 13).

Media milling is considered a good pretreatment of wood for enzymatic hydrolysis because of its ability to destroy the cell walls and reduce cellulose crystallinity (see Section 2.3.2). Torrefaction provides a good way of lowering the energy consumption required for obtaining a certain particle size, although special care has to be taken not to process the material for longer than is needed to obtain the limiting particle size, because the energy benefits due to torrefaction can be lost.
Fig. 31. Effect of mild torrefaction on the median particle size \(d_{50}\) as a function of \(\Delta^*\). Modified from Paper V, published by permission of De Gruyter.

Fig. 32. Effect of mild torrefaction on the median particle size \(d_{50}\) as a function of the total available impact energy of the grinding ball, \(E_T\). Modified from Paper V, published by permission of De Gruyter.

Table 12. Specific energy consumption and median particle sizes in the REF, TOR B and TOR C experiments. Paper V, published by permission of De Gruyter.

<table>
<thead>
<tr>
<th>SECoSc (kJ g(^{-1}))</th>
<th>(d_{50}) ((\mu)m) REF</th>
<th>TOR B</th>
<th>TOR C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.26</td>
<td>-</td>
<td>115 ± 6</td>
<td>79 ± 3</td>
</tr>
<tr>
<td>0.34</td>
<td>94.0 ± 1.1</td>
<td>53 ± 8</td>
<td>41 ± 5</td>
</tr>
<tr>
<td>0.51</td>
<td>44 ± 3</td>
<td>35 ± 3</td>
<td>32.6 ± 0.6</td>
</tr>
<tr>
<td>0.68</td>
<td>30 ± 3</td>
<td>26.6 ± 1.4</td>
<td>24.6 ± 0.7</td>
</tr>
<tr>
<td>0.86</td>
<td>23.3 ± 1.1</td>
<td>19.9 ± 0.8</td>
<td>18.7 ± 0.5</td>
</tr>
<tr>
<td>1.20</td>
<td>19.8 ± 1.0</td>
<td>17.0 ± 0.2</td>
<td>17.4 ± 0.2</td>
</tr>
<tr>
<td>1.71</td>
<td>13.8 ± 0.4</td>
<td>13.6 ± 0.4</td>
<td>12.9 ± 0.6</td>
</tr>
<tr>
<td>2.57</td>
<td>16.0 ± 0.0</td>
<td>14.5 ± 1.2</td>
<td>14 ± 2</td>
</tr>
</tbody>
</table>
Fig. 33. Effect of mild torrefaction on a) $\text{AR}_{50}$ and b) $\Delta \text{AR}$ as a function of the total available impact energy of the grinding ball. Modified from Paper V, published by permission of De Gruyter.

Table 13. Comparison of CrI and $d_{50}$ between REF and TOR C pretreated samples when pulverised for various lengths of time. Paper V, published by permission of De Gruyter.

<table>
<thead>
<tr>
<th>Milling time (min)</th>
<th>$E_T$ (J)</th>
<th>REF ($M_L = 0.0%$)</th>
<th>TOR C ($M_L = 2.8%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CrI (%)</td>
<td>$d_{50}$ (µm)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>44 ± 2</td>
<td>&lt; 4000$^a$</td>
</tr>
<tr>
<td>2</td>
<td>684</td>
<td>28 ± 2</td>
<td>94.0 ± 1.1</td>
</tr>
<tr>
<td>3</td>
<td>1027</td>
<td>17 ± 3</td>
<td>44 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>1711</td>
<td>11 ± 4</td>
<td>23.3 ± 1.1</td>
</tr>
</tbody>
</table>

$^a$ Feed was screened with a 4 mm sieve
6 Conclusions

Fine grinding of dry Norway spruce wood was studied using three types of fine grinding mills in which particle breakage takes place due powerful impacts: two types of non-media mill, known as the air classifier mill and the fluidised bed opposed jet mill, and one vibration-type media mill known as the oscillatory ball mill. These milling techniques proved capable of reducing the median particle size of dried Norway spruce wood to below 25 \( \mu m \).

The impact events occurring in the media mill were capable of producing very fine wood powders from dried Norway spruce that had a lower cellulose crystallinity and rounder shaped particles with a more uniform shape distribution than in dried Norway spruce wood pulverised to a similar particle size range by impact events occurring in non-media mills. In the case of the air classifier mill and fluidised bed opposed jet mill the speed of the classifier had the strongest effect on the physical properties of the resulting wood powders, whereas with the oscillatory ball mill the amount of feed, the weight of the grinding ball and the oscillation frequency had a significant influence on the physical properties of the wood. When Norway spruce wood was ground to a median particle size of less than 20 \( \mu m \) the use of more energy intensive impacts resulted in agglomeration and increased the temperature of the wood during further processing. Although the prolongation of media milling led to no further decrease in particle size, the wood particles continued to become rounder and more homogeneous in shape.

The classifier speed had the greatest effect on the energy consumption in air classifier and opposed jet milling, with a higher rotor speed in the air classifier mill and a higher grinding pressure in the opposed jet mill yielding an increase in the production rate when all the other operational parameters were kept constant. In the air classifier mill the specific electrical energy consumption for attaining a certain median particle size could be lowered by increasing the rotor speed, while in the opposed jet mill an increase in grinding pressure reduced the specific energy consumption but increased the eventual fineness when milling to a median particle size around 20 \( \mu m \). The energy consumption in oscillatory ball milling was affected by the amount of feed, in that a very low feed volume resulted in poor energy efficiency and an alteration in particle size reduction behaviour during milling. In the fluidised opposed jet mill the energy requirement for compression of the grinding air was over 32 \( kJ \ g^{-1} \) (approx. 9000 \( kWh \ t^{-1} \)) when pulverising dried Norway spruce wood with a median particle size of 199 \( \mu m \) (± 6 \( \mu m \)) down to a size between 48.2 \( \mu m \) and 69.2 \( \mu m \). In the air classifier mill dried
Norway spruce wood with a median particle size between 1 mm and 2 mm was pulverised down to 23.8 µm with a specific energy consumption of 15.5 kJ g⁻¹ (4310 kWh t⁻¹). Further optimisation would be possible in both mill types. A practical estimate for the minimum specific energy consumption in the impact-based media milling of dried Norway spruce wood, ignoring energy losses in driving the machine and additional equipment, would be that the median particle size could be reduced from 1–2 mm down to 100 µm with 0.36 kJ g⁻¹ (100 kWh t⁻¹) and down to 20 µm with 1.4 kJ g⁻¹ (380 kWh t⁻¹). The total energy consumption in media mills is higher than this, however, due to the consumption of energy that is not directed at the particles, a source of energy loss that is significantly influenced by the architecture of the mill.

Cryogenic grinding conditions can be used in impact-based media milling to obtain different powders from Norway spruce wood from those produced under ambient grinding conditions. Also, the energy efficiency of fine grinding can be enhanced by choosing cryogenic instead of ambient grinding conditions. Wood powders with a median particle size significantly lower than 13 µm were obtained when milling under cryogenic conditions, whereas this was not possible under ambient grinding conditions, and the reduction of cellulose crystallinity in an impact-based media mill exhibits a different behaviour pattern as a function of milling time under cryogenic in comparison to ambient conditions. On the other hand, moisture content has a stronger influence on the size and shape of the resulting particles when grinding is performed under ambient conditions. Thermal pretreatment by torrefaction can reduce the energy consumption required in impact-based media mills for attaining a certain particle size, provided that the targeted median particle size is not below 17.4 µm (± 0.2 µm). The specific energy consumption was typically reduced by more than 21% when the mass loss due to torrefaction was 2.8%. The shape of the particles and their cellulose crystallinity are not significantly affected by torrefaction pretreatment when considering similar levels of energy consumption and torrefied samples having a mass loss due to torrefaction of 2.8% or less.

The present findings suggest that the impact-based fine grinding of dried wood should be divided into media and non-media milling processes, depending on the final product. Media milling involves double impacts, which favour lowered cellulose crystallinity and rounder shaped particles by comparison with non-media mills. On the other hand, media mills can be used to obtain similar kinds of wood powders as produced with non-media mills, but then the raw material has to be moist rather than dry, which can cause different problems in
These processing problems and the energy consumption required for drying could be avoided by preferring cryogenic grinding conditions, but this also has a specific effect on the properties of the product. The fine grinding of Norway spruce wood with a median particle size in the millimetre region down to around 20 µm should be possible with an energy consumption of several hundred kilowatt-hours per tonne, but further optimisation work would be needed to achieve this specific energy consumption on an industrial scale. The fine grinding of wood to a median particle size below 20 µm should be considered with extreme caution, because the resistance of Norway spruce wood, for example, to particle size reduction increases quite suddenly in this particle size region and can lead to the formation of agglomerations.
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