Chapter 4

Physical Pretreatment − Woody Biomass Size Reduction − for Forest Biorefinery

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Physical pretreatment of woody biomass or wood size reduction is a prerequisite step for further chemical or biochemical processing in forest biorefinery. However, wood size reduction is very energy intensive which differentiates woody biomass from herbaceous biomass for biorefinery. This chapter discusses several critical issues related to wood size reduction: (1) factors affecting mechanical energy consumption and the post-pretreatment wood size-reduction approach to significantly reduce energy consumption, (2) biomass substrate specific surface area for substrate size characterization and the wet imaging technique for woody substrate size/specific surface measurements, (3) the effect of biomass substrate size/specific surface on enzymatic cellulose hydrolysis, and (4) the concept of substrate "surface productivity" for the determination of optimal degree of size reduction and energy efficient wood size reduction.

Keywords: woody/forest biomass; forest biorefinery; size reduction; enzymatic hydrolysis/saccharification; size characterization

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In Sustainable Production of Fuels, Chemicals, and Fibers from Forest Biomass; Zhu, J., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Introduction

Woody biomass represents a significant portion of biomass that can be sustainably produced in the United States (*1*) and around the world. Woody biomass has several advantages for the future biobased economy, such as high density that reduces transportation cost and flexible harvesting time that eliminates long-term storage, and low ash content that reduces processing dead load (*2*). To promote biodiversity and meet local and regional bioenergy needs, woody materials will be a critical part of the biomass supply mix in the future biobased economy.

Effective separation and fractionation of different components of woody biomass are critical to forest biorefinery. Woody biomass consists of various components, each of which can be used to produce a variety of bioproducts, including biofuel. For example, cellulose has been traditionally used to produce fiber to make pulp and paper through delignification. Cellulose can also be saccharified by enzymes to produce sugars to be converted to biofuel. However, wood is a structural material, physically large and structurally tough, and has natural resistance to microbial destruction. To improve wood cellulose accessibility to enzymes for biochemical conversion to sugars, physical and chemical barriers need to be removed. This is often achieved by pretreatment, a preprocessing step using mechanical, thermal, and thermo-chemical means (*2*). Physical pretreatment; i.e., wood size reduction through mechanical means, can increase the accessible surface area of wood cellulose to enzymes. This allows effective separation/fractionation for efficient utilization of different wood components through biorefining by chemical, thermal, and/or microbial processing (*3–5*).

Feedstock pretreatments reported in the literature have almost exclusively focused on chemical pretreatments. Physical pretreatment; i.e., biomass size reduction, has been largely overlooked. This is partly because most reported studies were focused on herbaceous biomass that does not need significant processing and energy to achieve desired size reduction (*6*). Such preprocessing of herbaceous biomass can be achieved during harvesting using combines. Whereas a certain degree of size reduction of woody biomass is possible during harvesting using modern technologies designed specifically for harvesting woody energy crops, it can only achieve the first step in size reduction (*2*, *4*), i.e., from trees or logs to wood chips. Size reduction of woody biomass is very similar to wood fiber production, which involves two steps (*2*, *4*). The first step is chipping logs or branches to produce wood chips with a size around 10–50 mm in two dimensions and 5–15 mm in the third dimension. The second step is fiberization or pulverization of wood chips to produce wood fibers/fiber bundles or flour. Wood chipping is a common practice in the pulp and paper industry, and energy costs are relatively low compared with those for fiberization or pulverization (*2*). Therefore, this chapter is dedicated to the second step, wood-size reduction, that directly affects the end products through subsequent processing: separation and fractionation.

Several well developed technologies are available for biomass size reduction, such as hammer milling, knife milling, shredding, and disk or attrition milling.

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Several studies reported biomass size reduction using these technologies (*6–9*). Early work on size reduction of woody biomass included those producing wood flour for manufacturing wood composites (*10*). Hammer and disk milling are the two predominant technologies from a large-scale production point of view. Hammer milling has been mainly used for producing wood flours for composites and pellets, whereas disk milling has been used for wood fiber production. Disk milling represents one of the best fiberization processes for woody feedstock in commercial fiber production at the scale of 1,000 tons/day, which is equivalent to an ethanol production capacity of 100 million L/year. The fiberization process of disk milling is favorable for efficient enzymatic saccharification (*4*). Therefore, we will focus on disk milling in the following discussion.

Energy Consumption in Wood Size Reduction

Wood-size size reduction is energy intensive, which makes physical pretreatment of woody biomass particularly important. For example, typical electrical–mechanical energy consumption for disk milling wood chips under atmospheric conditions to the level of fibers/fiber bundles is about 150–800 kWh (or 0.54–2.88 GJ)/ton wood (*3*, *8*). Energy consumption to produce wood chips is about 50 kWh (0.18 GJ)/ton wood. The total thermal energy of ethanol produced from wood is estimated at 7.2 GJ/ton wood based on an ethanol yield of 300 L/ton of od wood with current technology and a higher heating value of ethanol of about 24 MJ/L. Therefore, size-reduction energy consumption is about 10 to 40% of the thermal energy of ethanol produced from wood. Considering the conversion efficiency of 30% from thermal energy to electric–mechanical energy consumed in wood-size reduction, the thermal energy in ethanol produced from wood is just sufficient for wood-size reduction. Because energy is the major product of a biorefinery operation, one has to achieve good net energy output in addition to profitability, or it will be necessary to seek energy elsewhere. Therefore, significant reduction in energy consumption for wood-size reduction, preferably by a factor of 5–10 to about 0.1–0.4 GJ/ton, is required to achieve sensible net energy output from wood ethanol production. This requirement poses a significant challenge to biofuel production from woody biomass.

Several factors affect energy consumption for wood-size reduction through disk milling (*2*). The first and foremost factor is the fiberization mechanism. It is well understood that energy consumption in mechanical wood pulping depends significantly on how the wood chips are fiberized (*2*). Depending on the disk-milling conditions, wood chips can be fractured through the lumen of wood tracheids, such as in producing refiner mechanical pulps (RMP) under atmospheric conditions. Wood chips can also be fractured in the S1 and S2 layer of cell wall when wood chips are steam pretreated, such as in producing thermomechanical pulps (TMP) in which low-pressure steam of about 2-4 bar (~120-140°C) is used to soften wood chips before disk refining. When the steam pressure is increased to 7.2 bar, as the steam temperature (~166°C) exceeds the glass transition temperature of lignin (*11*), wood chips are fractured in the lignin-rich middle lamella (ML). This high-pressure treatment of wood chips

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is used to produce medium-density fiberboard pulps (MDF). Figure 1 shows the schematic diagram of different wood chip fiberization mechanisms. The mechanical energy consumption varies significantly among different fiberization mechanisms.

Typical energy consumption in the first pass refining of wood chips for producing RMP, TMP, and MDF are about 800, 500, and 150 kWh/ton oven-dry (od) wood based on numerous laboratory experiments and pulp mill commercial practice (*2*). The energy consumption in first pass refining of chemically pretreated wood chips (CTMP) is often lower than that for TMP. The surface chemical compositions of the pulp fibers produced by different fiberization mechanisms are very different. RMP exposes mostly cellulose on fiber surfaces, whereas MDF fibers are coated with lignin on their surface. This can be clearly seen from the color of these pulps with RMP being the lightest and MDF being browner and darker. The difference in surface chemical composition certainly affects cellulose enzymatic saccharification, as revealed in our previous study (*4*).

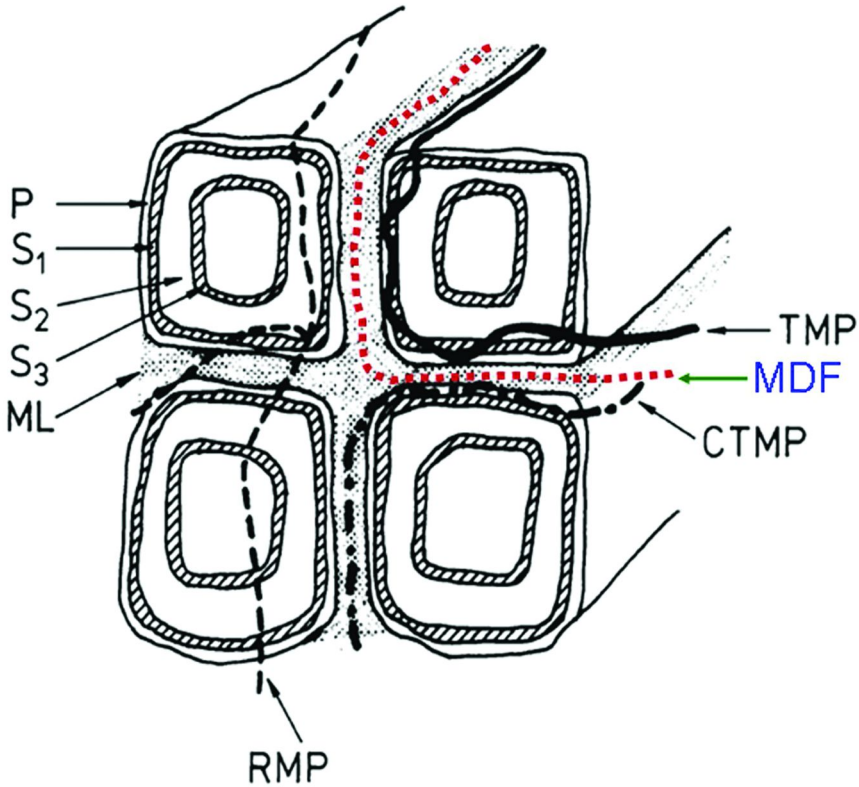

*Figure 1. A schematic diagram showing the various fiberization mechanisms of softwood. Adapted with permission from Franzen, Nordic Pulp Paper Res. J., **1**:4, 1986 and Salmen, Fundamentals of Mechanical Pulping, in Book 5: Mechanical Pulping, Papermaking Science and Technology, Gullichsen and Paulapuro Eds., Fapet Oy, Finland, 1999. Copyrights 1986 Nordic Pulp and Paper Research Journal and 1999 Finland Paper Engineers' Association.*

The second factor affecting energy consumption for wood size reduction is the degree of size reduction. Generally speaking, more energy is required to produce substrate with a large surface area (fine material). Characterization of biomass substrate is necessary to fully address this issue. Unfortunately, proper characterization of biomass substrate size is a difficult task, as will be discussed later.

Disk milling conditions certainly affect energy consumption for wood size reduction. Conditions can alter wood chip fiberization mechanism, as discussed previously. They can also affect the substrate morphology and size and thereby affect energy consumption without affecting fiberization mechanism. For example, opening the disk-plate gap in refining results in low energy consumption, and a coarse substrate that may contain fiber bundles (*3*). One study demonstrated that in mechanical pulping, the disk-refining (milling) process conditions can significantly affect disk-refining energy consumption (*12*). However, the energy savings that can be realized without sacrificing pulp quality is very limited in mechanical pulping (*13*). For example, decreasing primary-stage disk-refining discharge consistency (the same as solids-loading) from 50 to 38% only resulted in 7% energy savings in commercial-scale trial runs (*14*). However, the fiber qualities required for papermaking are not an issue for woody biomass saccharification. This makes it feasible to optimize milling process conditions to significantly decrease energy consumption for wood-size reduction while maximizing the enzymatic cellulose saccharification efficiency under nominal chemical pretreatment conditions.

Our recent study using lodgepole pine found that reducing solids-loading in disk milling from 30% (the solids of the wood chips right after pretreatment) to about 20% can reduce disk-milling energy by 20% (*3*). We also found that opening the disk-plate gap from 0.38 mm to 1.52 mm can reduce disk milling energy by 75% (or a factor of 4) when wood chips were pretreated by dilute acid or the Sulfite Pretreatment to Overcome Recalcitrance of Lignocelluloses (SPORL) process (*3*). No negative effects on the enzymatic saccharification of the resultant substrates were observed in the ranges of disk-milling solids loading and disk plate gaps (0.38-1.52 mm) studied (*3*). Near complete saccharification was achieved for lodgepole pine pretreated by SPORL followed by disk milling with energy consumptions of 20–50 kWh/ (0.07-0.18 GJ/ton).

Post-Pretreatment Wood-Size Reduction

The approach of biomass size reduction prior to chemical pretreatment has been proposed as the standard process flow for biofuel production by several key pieces of the literature (*15*, *16*) and by the recent U.S. Department of Energy biofuels research roadmap (*17*). This approach has a significant negative effect on the overall energy balance and net energy output in biofuel production from woody biomass because wood-size reduction is very energy intensive. As discussed in the previous section, thermal or chemical pretreatment of wood chips can alter the wood chip fiberization mechanism in disk milling and thereby reduce wood chip size-reduction energy consumption (comparing RMP, TMP,

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and CTMP). Furthermore, these pretreatments can also alter the chemical composition and physical structure of wood by partially removing and modifying some cell-wall components such as hemicellulose and lignin, which can lead to reduced energy consumption for milling the pretreated wood. We therefore have proposed to conduct size reduction after chemical pretreatment, i.e., post-chemical pretreatment size reduction, as shown in Figure 2, to significantly reduce the energy consumption for wood-size reduction (*2*, *3*, *5*, *18*).

This approach is also used in steam explosion pretreatment through the post-steam-pretreatment discharge (flashing or explosion) process. Energy savings of about 30% were obtained in mechanical pulping of papermaking fibers when wood chips were pretreated by oxalic acid to partially remove wood hemicelluloses (*19*). Table I lists energy savings in mechanical milling of lodgepole pine wood chips pretreated by different chemical pretreatments. A factor of 4 savings in size-reduction energy consumption was achieved when a SPORL process (*18*, *20*) was applied to lodgepole pine wood chips. Furthermore, near complete enzymatic saccharification was achieved for the substrates from disk-milling lodgepole (softwood) wood chips pretreated by the SPORL process. The energy consumption for the disk milling of a SPORL (pH = 1.9) pretreated wood chips reported in Table I and our previous work are equivalent to that used for size reduction by steam explosion. The thermal energy used for size-reduction through flashing by steam explosion can be estimated to approximately 0.4 GJ/ton wood by using the difference in enthalpy between saturated steam and saturated water with consideration of thermal enery recovery in the form of low pressure steam and hot water, respectively. It should be pointed out that the total energy consumption for conducting steam explosion at 215ºC is estimated at 1.8 GJ/ton wood (*2*) and used for both thermal pretreatment and size redudction.

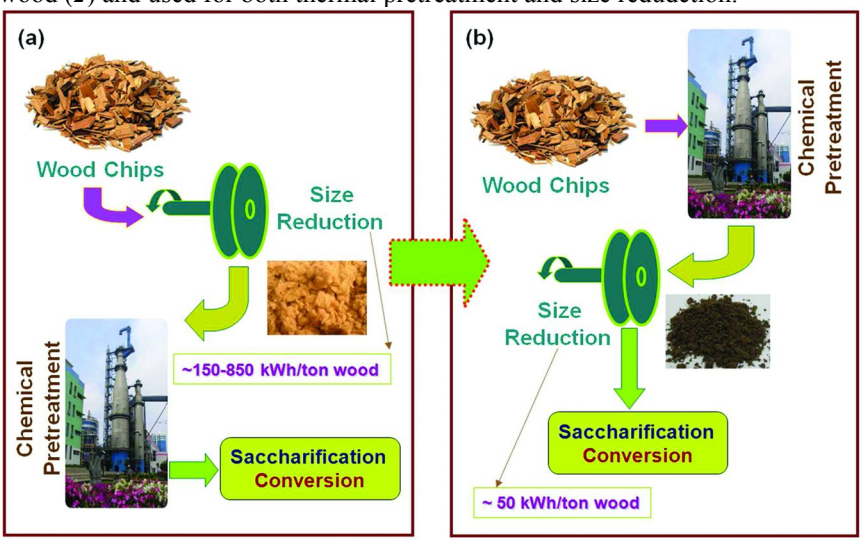

Figure 2. Schematic diagram shows the approach for mechanical wood size-reduction operation from (a) pre- to (b) post-chemical pretreatment to reduce energy consumption. Reproduced from reference (5).

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Table I. Effects of chemical pretreatment on lodgepole pine wood chip size-reduction energy consumption and the resultant substrate enzymatic digestibility (SED). Pretreatment liquor to wood rato (L/W) = 3, disk milling solids loading = 30% (≈ the solid contents of pretreated wood chips), and disk plate gap = 0.76 mm. Reproduced from reference (*5*)

Pretreatment @180°C for 30 min[a]	*Initial liquor pH*	*Disk milling energy (kWh/ton wood)*	*Size-reduction energy savings (%)*	*SED (%)*
Untreated		699		12.7
Hot-water	5.0	680	2.7	16.0
Acid	1.1	412	41.0	41.6
SPORL	4.2	594	15.0	75.1
SPORL	1.9	153	78.1	91.6

[a] Sodium bisulfite charge was 8% on oven dry (od) wood for the two SPORL runs; sulfuric acid charge was 2.21 (w/w) on od wood for the dilute acid and low pH SPORL runs, and 0 for the hot-water and high pH SPORL runs.

The post-chemical pretreatment size-reduction approach has several benefits: (1) it significantly reduces mechanical energy consumption for wood-size reduction by taking advantage of chemical pretreatments to remove solid wood mass and soften wood structure; (2) it avoids the difficult and energy-intensive operation of mixing high-consistency pulp (size-reduced/fiberized woody material) with chemicals during pretreatment; (3) it also avoids the difficult solid (fibers) and liquid (pretreatment hydrolysate) separation process after pretreatment; and (4) it affords a low liquid to woody biomass ratio in thermo-chemical pretreatments, which reduces thermal energy consumption and potentially produces a concentrated hemicellulose sugar stream favorable for fermentation and reducing downstream separation and distillation cost; the liquid uptake of wood chips is much lower than fibers and/or fiber bundles because of the porous and hydrophilic nature of wood fibers.

Substrate Size Characterization

Proper characterization of substrate size is important to determine the degree of wood size reduction that affects not only energy consumption but also enzyme accessibility and therefore substrate enzymatic digestibility. The particle-size distribution of a given substrate can be measured by a variety of techniques. The traditional techniques are the sieve and screen methods. Modern techniques include imaging analysis. Imaging techniques often measure the projection dimensions of a particle. The geometric mean diameter of the particles has commonly been used to characterize biomass substrate (*9*). This is probably because size measurements were often carried out by traditional sieve or screen methods (*6*, *9*). This size measure is significantly affected by biomass substrate morphology such as particle aspect ratio (*4*). Depending on the size-reduction

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method used, the same mesh size can mean completely different particles. For example, the fraction of hammer-milled spruce (HM-R80) passing a 48 mesh screen and being retained on an 80 mesh screen is much coarser (larger in size) than the fraction retained on a 48 mesh screen from the disk milling (DM-R48) of the same wood, as shown in Figure 3. Most size-reduction processes produce fibrous substrate with wide ranges of particle (fiber) aspect ratios over 10. As a result, existing data on substrate size characterization using sieve and screen methods have limited value.

Substrate surface area is most relevant to heat and mass transfer, enzyme accessibility, and energy consumption; therefore, the substrate-specific surface should be used to characterize the size of a substrate. Specific surface area has been used to correlate energy consumption for comparing the efficiencies of several size-reduction processes (*7*). The calculation of specific surfaces was based on the assumption that the substrate consists of spherical particles. Under this assumption, the physical dimension is often represented by its mean diameter. Several statistical ways can calculate the mean particle diameter. The arithmetic mean D_{10}, Sauter mean D_{32}, and volume (mass) mean D_{30} diameters can be calculated (*21*, *22*). Neglecting particle surface roughness, the external volumetric specific surface, S_p^V, can be estimated according to the equation

$$S_p^V = \frac{A_p}{V_p} = 6 \cdot \frac{\sum_i n_i d_i^2}{\sum_i n_i d_i^3} = \frac{6}{D_{32}} \qquad (1)$$

where A_p, and V_p are the total surface area and volume of the particles, respectively, and n_i is the number of particles in size bin i with representative diameter d_i. D_{32} is also called Sauter mean diameter (*SMD*). By measuring the oven dry weight of the sample, m_p, before analysis, the specific surface, S_P, of the sample can be determined using the following expression when each fiber (particle) in the sample is accounted for and measured:

$$S_p = \frac{A_p}{m_p} = \frac{\pi \sum_i n_i d_i^2}{m_p} \qquad (2)$$

The spherical model is not suitable for biomass substrate as biomass particles are not spheres but shives or spindles with very large aspect ratios (Figures 3 and 4). The substrates derived from disk-milling processes typically have an aspect ratio of 50 to 100. Therefore, measurements in more than one dimension are required to estimate substrate-specific surface by using non-spherical particle models. Furthermore, measurements need to be carried out under wet conditions, as enzymatic hydrolysis of lignocelluloses is always conducted in aqueous solutions. The wet-imaging technique is a technology that is commercially available and has been widely applied in pulp and paper science for fiber length characterization. When the spatial resolution of the image system is

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increased to resolve the width or diameter of a fiber, the system can be used for two-dimensional characterization of a lignocellulosic substrate. Assuming individual fibers are cylinders and neglecting surface roughness, the volumetric specific surface of fibers, S_p^V, can be estimated according to the following equation (*4*),

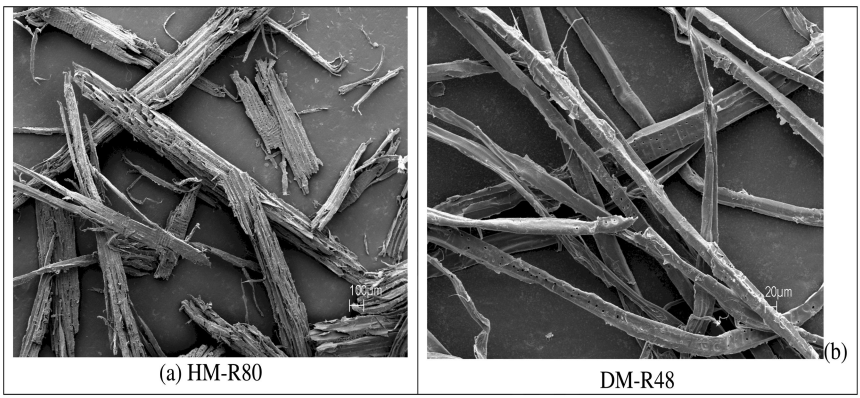
$$S_f^V = \frac{A_f}{V_f} = \frac{2\sum_i n_i(d_i^2 + 2\cdot d_i \cdot L_i)}{\sum_i n_i d_i^2 \cdot L_i} = \frac{4\sum_i n_i d_i (L_i + d_i/2)}{\sum_i n_i L_i \cdot d_i^2} \quad (3)$$

For most fibers with aspect ratios greater than 5, Eq. (3) can be approximated to

$$S_f^V \approx 4\cdot\frac{\sum_i n_i L_i \cdot d_i}{\sum_i n_i L_i \cdot d_i^2} = \frac{4}{D_{L21}} \quad (4)$$

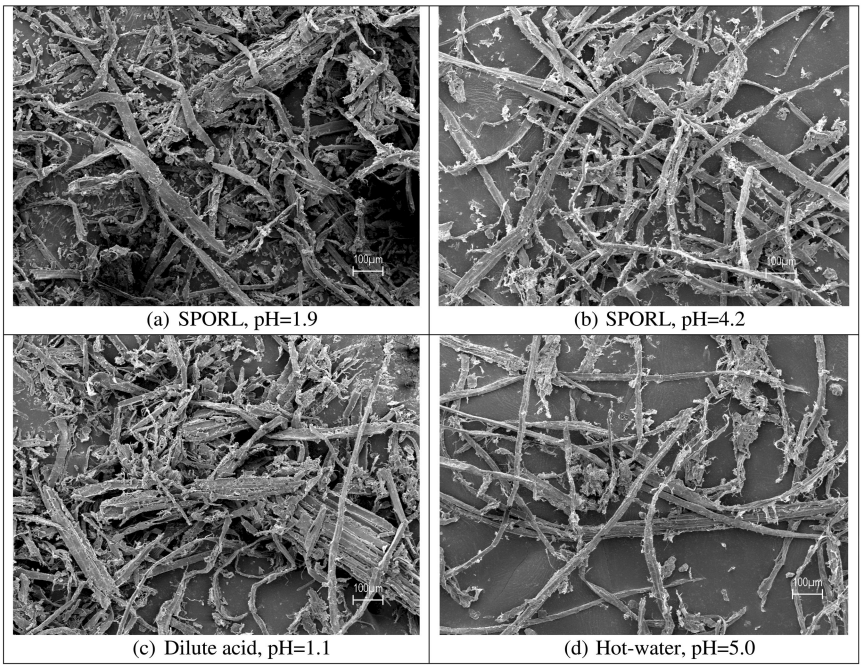
where A_f and V_f are the total surface area and volume of the fibers, respectively. n_i is the number of fibers in fiber group i. L_i and d_i are the representative length and diameter of fiber group i, respectively. D_{L21} is a fiber-length weighted-surface-length mean fiber diameter or "width." Similarly, the specific surface of the sample, S_f, can be determined by measuring the oven dry weight of the sample, m_f, before analysis when each fiber (particle) in the sample is accounted for and measured:

$$S_f = \frac{A_f}{m_f} = \frac{\pi}{2}\frac{\sum_i n_i(d_i^2 + 2\cdot d_i \cdot L_i)}{m_f} \approx \pi\frac{\sum_i n_i \cdot d_i \cdot L_i}{m_f} \quad (5)$$



(a) HM-R80 | DM-R48

Figure 3. Comparison of the morphology of spruce substrates produced from hammer milling (HM) and disk milling (DM), (a) HM-R80, (b) DM-R48. Reproduced from reference (4).



(a) SPORL, pH=1.9 (b) SPORL, pH=4.2

(c) Dilute acid, pH=1.1 (d) Hot-water, pH=5.0

Figure 4. SEM images of lodgepole pine substrates produced from different pretreatment process and then disk milled at solids content of 6% with disk plate gap of 0.76 mm. The pH values were measured from the initial pretreatment liquor.

Certainly, the assumption of cylinder is an oversimplification. Fibers have lumens. A hollow cylindrical fiber with a very thin wall thickness is a more realistic assumption. Ignoring the wall thickness, the specific surface is simply two times the specific surface of a cylinder (Eqs. 3 and (5). When chemical pretreatment such as Kraft pulping is applied, the fiber lumen can collapse and the fiber is more like a ribbon with a rectangular cross section (Figure 4). Tables II and III list the suitable expressions for estimating specific surfaces of different fiber cross-sectional shapes, along with the relative deviations from the cylinder assumption (Eqs. 3 and (5) (*23*). Certainly, the relative deviation in specific surface based on the cylinder model from the actual value is a function of the cross section of a fiber. This can be clearly seen from Table II, and especially from Table III for ribbon type fibers, and fibers having elliptical cross sections with various ratios of major and minor axial dimensions (d and w are the dimensions of the two major axes of the cross section). Fortunately, fibers can freely spin in suspension during wet imaging, and therefore, the probabilities of imaging different orientations of a non-cylindrical fiber are the same. As a result, the relative deviation in the measured mean fiber specific surface from that obtained using the cylinder model (with the diameters equal to the measured projection dimensions d_i as listed in Tables II and III) will be significantly smaller than the deviations listed in Tables II and III, when tens of thousands fibers are measured.

Table II. Equations to calculate the average (volumetric) specific surface of a substrate using fiber models of different cross sections. The measured width (diameter), *d*, is the image projection dimension.

Fiber cross section	Circle	ELT-I	ELT-II	Square	Diamond
Imaging → Projection direction					
S_f^V	$\frac{4\sum_i n_i d_i (L_i + d_i/2)}{\sum_i n_i L_i \cdot d_i^2} \approx 4 \cdot \frac{\sum_i n_i L_i \cdot d_i}{\sum_i n_i L_i \cdot d_i^2} = \frac{4}{D_{L21}}$	$\frac{6\sum_i n_i d_i (L_i + d_i/3)}{\sum_i n_i L_i \cdot d_i^2} \approx 6 \cdot \frac{\sum_i n_i L_i \cdot d_i}{\sum_i n_i L_i \cdot d_i^2} = \frac{6}{D_{L21}}$	$\frac{4\sqrt{3}\sum_i n_i d_i (L_i + d_i/2/\sqrt{3})}{\sum_i n_i L_i \cdot d_i^2} \approx 4\sqrt{3} \frac{\sum_i n_i L_i \cdot d_i}{\sum_i n_i L_i \cdot d_i^2} = \frac{4\sqrt{3}}{D_{L21}}$	$\frac{4\sum_i n_i d_i (L_i + d_i/2)}{\sum_i n_i L_i \cdot d_i^2} \approx 4 \cdot \frac{\sum_i n_i L_i \cdot d_i}{\sum_i n_i L_i \cdot d_i^2} = \frac{4}{D_{L21}}$	$\frac{4\sqrt{2}\sum_i n_i d_i (L_i + d_i/2/\sqrt{2})}{\sum_i n_i L_i \cdot d_i^2} \approx 4\sqrt{2} \cdot \frac{\sum_i n_i L_i \cdot d_i}{\sum_i n_i L_i \cdot d_i^2} = \frac{4\sqrt{2}}{D_{L21}}$
S_f	$\frac{\frac{\pi}{2}\sum_i n_i (d_i^2 + 2 \cdot d_i \cdot L_i)}{m_f} \approx \pi \frac{\sum_i n_i \cdot d_i \cdot L_i}{m_f}$	$\frac{2\sqrt{3}\sum_i n_i d_i (L_i + d_i/3)}{m_f} \approx 2\sqrt{3} \frac{\sum_i n_i \cdot d_i \cdot L_i}{m_f}$	$\frac{3\sum_i n_i d_i (L_i + d_i/2/\sqrt{3})}{m_f} \approx 3 \frac{\sum_i n_i \cdot d_i \cdot L_i}{m_f}$	$\frac{4\sum_i n_i d_i (L_i + d_i/2)}{m_f} \approx 4 \frac{\sum_i n_i \cdot d_i \cdot L_i}{m_f}$	$\frac{2\sqrt{2}\sum_i n_i d_i (L_i + d_i/2/\sqrt{2})}{m_f} \approx 2\sqrt{2} \frac{\sum_i n_i \cdot d_i \cdot L_i}{m_f}$
Characteristic Size	$D_{L21} = \frac{\sum_i n_i L_i \cdot d_i^2}{\sum_i n_i L_i \cdot d_i}$	$D_{L21} = \frac{\sum_i n_i L_i \cdot d_i^2}{\sum_i n_i L_i \cdot d_i}$	$D_{L21} = \frac{\sum_i n_i L_i \cdot d_i^2}{\sum_i n_i L_i \cdot d_i}$	$D_{L21} = \frac{\sum_i n_i L_i \cdot d_i^2}{\sum_i n_i L_i \cdot d_i}$	$D_{L21} = \frac{\sum_i n_i L_i \cdot d_i^2}{\sum_i n_i L_i \cdot d_i}$
Relative difference in S_f^V to Circle		50%	73%	0	41%
Relative difference in S_f to Circle		10%	-5%	27%	-10%

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Table III. Equations to calculate the average (volumetric) specific surface of a substrate using columns of different cross sections of rectangles or ellipses with different ratios of width to thickness or major to minor axis, x= d/w

Fiber cross section	Rectangle d/w=x	Ellipse d/w=x
Imaging Projection direction →		
S_f^V	$\frac{2\sum_i n_i d_i[(x+1)L_i + d_i]}{\sum_i n_i L_i \cdot d_i^2}$ $\approx 2(x+1)\cdot\frac{\sum_i n_i L_i \cdot d_i}{\sum_i n_i L_i \cdot d_i^2} = \frac{2(x+1)}{D_{L21}}$	$\frac{2\sum_i n_i d_i\{[3(x+1)-\sqrt{(3x+1)(x+3)}]L_i + d_i\}}{\sum_i n_i L_i \cdot d_i^2}$ $\approx 2[3(x+1)-\sqrt{(3x+1)(x+3)}]\frac{\sum_i n_i d_i L_i}{\sum_i n_i L_i \cdot d_i^2}$ $= \frac{2[3(x+1)-\sqrt{(3x+1)(x+3)}]}{D_{L21}}$
S_f	$\frac{2\sum_i n_i d_i[(x+1)L_i + d_i]/x}{m_f}$ $\approx 2(1+\frac{1}{x})\frac{\sum_i n_i \cdot d_i \cdot L_i}{m_f}$	$\frac{\pi}{2}\frac{\sum_i n_i d_i\{[3(x+1)-\sqrt{(3x+1)(x+3)}]L_i + d_i\}/x}{m_f}$ $\approx \frac{\pi}{2x}[3(x+1)-\sqrt{(3x+1)(x+3)}]\frac{\sum_i n_i d_i L_i}{m_f}$
Characteristic size	$D_{L21} = \frac{\sum_i n_i L_i \cdot d_i^2}{\sum_i n_i L_i \cdot d_i}$.	$D_{L21} = \frac{\sum_i n_i L_i \cdot d_i^2}{\sum_i n_i L_i \cdot d_i}$
Relative difference in S_f^V to circle	$\frac{x-1}{2} * 100\%$	$\frac{(3x+1)-\sqrt{(3x+1)(x+3)}}{2} * 100\%$
Relative difference in S_f to circle	$\frac{2}{\pi}(2-\frac{\pi}{2}+\frac{1}{x}) * 100\%$	$\frac{x+3-\sqrt{(3x+1)(x+3)}}{2x} * 100\%$

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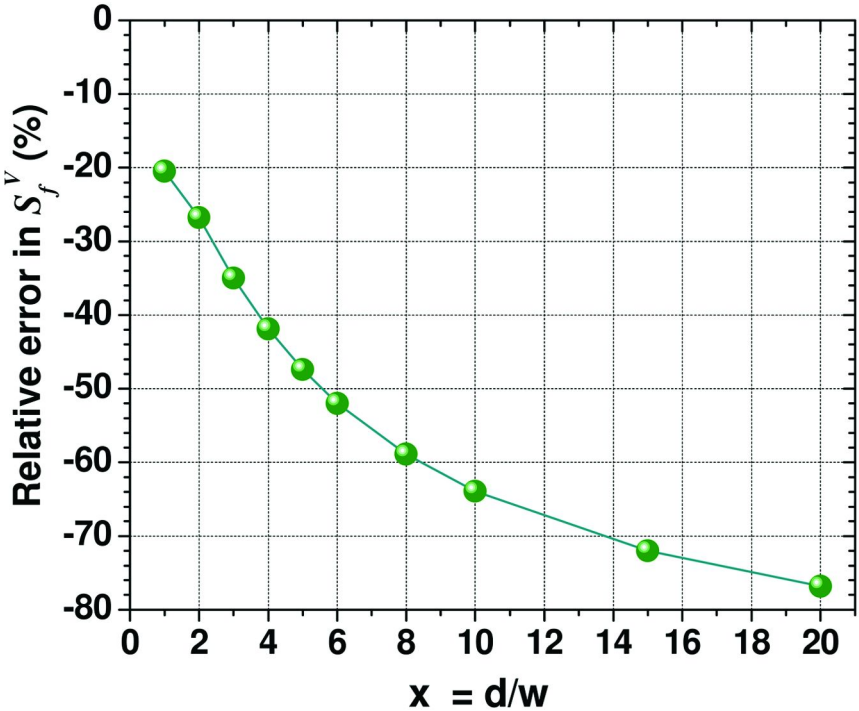

Figure 5. Estimated measurement errors between specific surface measurements of fibers with rectangular cross sections (width d and thickness w) and a circular cross section model using wet imaging techniques .

Figure 5 shows the estimated measurement errors in volumetric specific surfaces between those determined using the cylinder model with equal probability integration (average) over all orientations for ribbon fibers of width *d*, thickness, *w*, and their actual specific surfaces. The results clearly show that the wet imaging measured specific surfaces (integrated over all orientations) are in the same order of magnitude of actual specific surfaces. Most substrate fibers produced for biorefining applications would not be expected to have cross sections with a very large aspect ratio, x, of more than 20, as shown in Figure 4. This is not to deemphasize the errors caused by the geometric shape of fiber cross section using the wet imaging technique described here, but rather to illustrate that the wet imaging technique is probably the best approach currently available to address biomass substrate characterization, a very difficult problem.

Effect of Biomass Substrate Size on Enzymatic Hydrolysis Efficiency

Research has recognized that enzyme accessibility to substrate cellulose is a leading contributing factor to substrate enzymatic digestibility (*24*, *25*). It is also generally understood that substrate surface area directly affects the enzyme accessibility to cellulose and therefore, substrate surface area is a mass transfer

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limiting factor. However, limited studies have reported the effect of substrate size on cellulose to glucose conversion through enzymatic hydrolysis. In one of those, Rivers and Emert concluded that the particle size of substrates derived from ball milling had no effect on hydrolysis yield in the wet particle-size range of 0.25 to 0.47 mm (*26*). However, others reported that initial wood-chip size can affect cellulose saccharification even when the substrates were obtained after steam explosion of wood chips (*27*, *28*). Particle size also affected enzymatic digestibility of Ammonia Fiber/Freeze Explosion- (AFEX-) pretreated corn stover (*29*). Furthermore, particle size and surface area also affect the rate of hydrolysis (*30*).

Dasari and Berson found that glucose conversion of red-oak sawdust was almost doubled when particle size was reduced from 590–850 to 33–75 μm (*31*). Although the internal pore surface contributed to over 90% of the total surface of a microcrystalline cellulose, substrate hydrolysis efficiency was not affected by the internal pore surface area but rather by the substrate size or external surface (calculated with spherical particle assumption) (*32*). Sangseethong and others suggested that the enzyme-accessible internal pore surface depends on the pore depth dictated by the substrate size. As a result, this study concluded that particle size can affect enzymatic saccharification. Lack of accurate characterization of substrate size as discussed in the previous section can be a contributing factor to the different conclusions in the literature. Another factor may be related to the variability of different substrates used in the literature. It is expected that size effect on enzymatic hydrolysis of cellulose may be more important to untreated lignocellulosic substrates (*4*, *31*) than to pretreated substrates (*3*, *26*) under certain conditions. This will be further elaborated in the following discussions.

Many factors affect enzyme accessibility to substrate cellulose. The total substrate surface area is a representation of potentially accessible area to enzymes. Because of chemical barriers, not all surface areas are "productively" accessible to enzymes. The term "productive" refers to direct interactions between enzymes and cellulose that leads to cellulose hydrolysis. This term is used similarly to the term "non-productive adsorption" of enzymes by non-cellulose such as lignin in lignocellulosic substrate. When surface area is no longer a limiting factor or other factors become dominant, further increases in surface area or reduced substrate size will not significantly affect substrate enzymatic digestibility (SED). When comparing SEDs of fractionated substrates from a spruce thermo-mechanical pulp (TMP), we found that SED increased as substrate specific surface increased up to a certain level, but further specific surface increases did not result in the increase of SED (*4*). This is because the chemical barrier (such as hemicelluloses) becomes a dominant factor, or specific surface is no longer the limiting factor, for the spruce TMP when SED reaches about 20% (*4*). This is also observed from a set of substrates produced from disk milling using different disk plate gaps of the same chemically pretreated lodgepole pine wood chips (*3*). The effect of disk plate gap on enzymatic hydrolysis glucose yield is minimal when the disk plate gap is reduced to less than 1.5 mm, i.e., the substrate is sufficiently fine.

To illustrate this point, Figure 6 plots the SEDs for the two sets of substrates produced from disk milling of dilute acid and SPORL pretreated lodgepople pine wood chips (*3*), respectively. The low constant SEDs of about 40% of the dilute

acid samples produced using disk plate gaps from 0.38 to 3.8 mm indicate that dilute acid is not able to remove the recalcitrance of lodgepole pine. Chemical barrier is the dominant factor to enzymatic cellulose saccharification. As a result, size reduction to very fine substrates using very small disk plate gaps was not able to increase SED. The high SEDs of over 90% of the SPORL samples produced using disk plate gaps less than 3.8 mm suggest that SPORL effectively removed the chemical barriers, and furthermore, size reduction using a disk plate gap of about 3.8 mm was sufficient to remove the remaining barriers of substrate cellulose accessibility to cellulase. Therefore, the degree of size reduction achieved at a disk plate gap of 3.8 mm was close to maximal. Further reduction of the disk plate gap can no longer improve SED, as SED is already in the 90th percentile. However, increasing the disk plate gap resulted in small reductions in SED in general as expected. Because size-reduction energy consumption often increases with specific surface exponentially (*7*), this suggests that it is not cost effective to produce an extremely fine substrate in size reduction. There may be an optimal degree of size reduction for a given chemically pretreated biomass, as will be further elaborated in the next section.

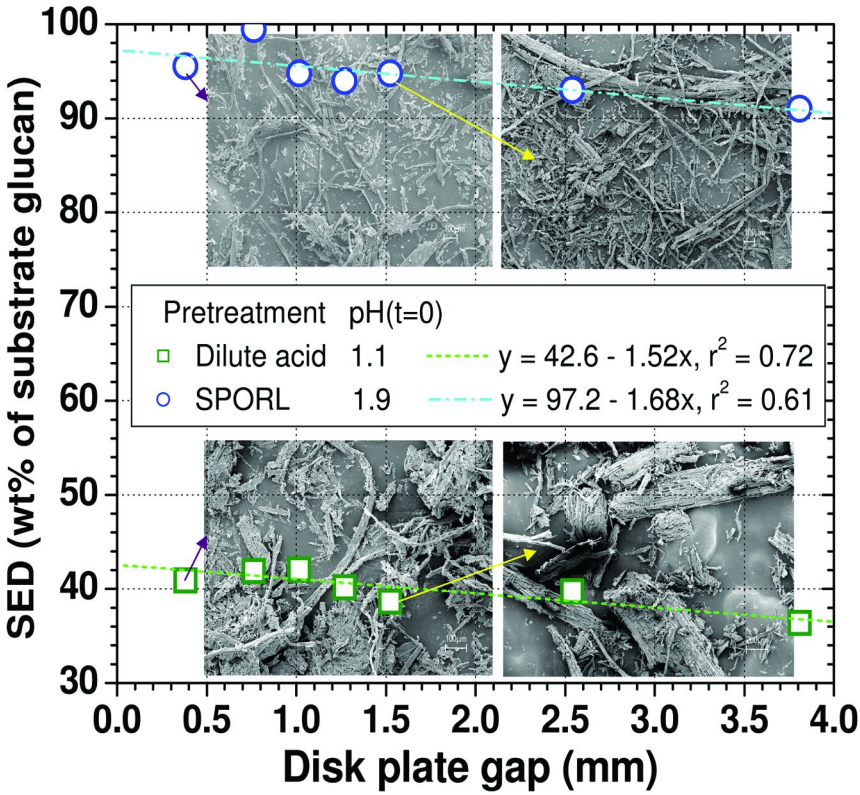

Figure 6. Effects of disk refining disk plate gap on substrate size/morphology and substrate enzymatic digestibility (SED).

Optimal Degree of Wood-Size Reduction and Size-Reduction Energy Efficiency

The term of "productive" substrate surface area illustrates the limit of size reduction on improving SED. The competing barriers to substrate enzymatic cellulose saccharification suggest there may be an optimal degree of size reduction, beyond which the "surface productivity" of the substrate decreases. The "surface productivity" can be expressed as the enzymatic hydrolysis glucose yield (EHGY) per unit surface area of the substrate, or simply the unit surface glucose yield as defined in our previous study (*4*), i.e.,

$$Surface\ Productivity = \frac{EHGY\ (g)}{Substrate\ surface\ area\ (m^2)} = \frac{EHGY\ (wt\%\ of\ substrate)}{Substrate\ specific\ surface\ (\frac{m^2}{g})} \tag{6}$$

The optimal degree of size reduction, or optimal specific surface, corresponds to the maximal Surface Productivity. Our previous study (*4*) found that the optimal degree of size reduction was about 0.1 ($\mu m^2/\mu m^3$) for a TMP spruce pulp. To achieve energy efficient biomass size reduction, size reduction should be conducted close to this optimal degree, and more specifically, slightly beyond this degree of size reduction because EHGY still increases beyond this degree, although surface productivity decreases.

A size-reduction energy efficiency can be defined as the glucose yield on unit size-reduction energy consumption (*4*), similar to the definition of pretreatment energy efficiency (*2*, *5*),

$$\text{Size} - \text{reduction energy efficiency} = \frac{EHGY\ (kg)}{\text{Size} - \text{reduction energy}\ (GJ)} \tag{7}$$

When comparing the performance of various size-reduction technologies or processes, both the size-reduction energy efficiency defined above along with EHGY should be used. Pretreatment can significantly affect the size-reduction energy efficiency by (1) reducing the energy consumption as discussed early in this chapter and (2) increasing enzymatic hydrolysis glucose yield caused by removing feedstock recalcitrance. One could define the size-reduction efficiency using the total substrate surface area divided by the size-reduction energy consumption. However, this definition does not take the issue of "non-productive surface" into account.

Summary

Wood-size reduction is very energy intensive and can significantly affect the overall energy efficiency of forest biorefinery. The post-pretreatment size-reduction approach can significantly reduce energy consumption for wood size reduction to the level equivalent to those used for herbaceous biomass. The degree of size reduction can not only affect energy consumption in size reduction, but can also affect enzymatic saccharification of biomass substrate. However,

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proper characterization of the size of biomass substrate is very difficult. Wet imaging analysis is probably the best available approach to effectively determine biomass substrate size. The specific surface-derived characteristic length (D_{L21}), fiber length weighted-surface-length mean fiber diameter or width, should be used to characterize biomass substrate. Not all substrate surfaces are productive for enzymatic hydrolysis. The concept of "Surface Productivity" defined as the enzymatic hydrolysis glucose yield (EHGY) on unit substrate surface can be used to describe the effectiveness of size reduction. Competing processes can affect enzymatic hydrolysis. When substrate surface is not the limiting factor to cellulose hydrolysis, further reducing substrate size will not result in improvement in cellulose saccharification. There is an optimal degree of wood size reduction, which should be close to the specific surface corresponding to the maximum "surface productivity."

Acknowledgments

This work was conducted on official government time. It is in the public domain in the United States.

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