Chapter 4

Effect of Press-Drying Parameters on Paper Properties

Ahmed Koubaa and Zoltan Koran

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.76508

Abstract

This study investigates alternatives that can improve the internal bond strength (IBS) of paper by pulp refining and paper press-drying (PD). The improvement mechanisms of IBS and their impact on the strength development of high-yield pulps are discussed. All experiments were conducted using a factorial design where the factors were four pulp types (one spruce thermomechanical (TMP) and three chemi-thermomechanical (CTMP) from spruce, birch, and aspen), three refining levels, three PD temperatures and three pressures. The effects of these treatments on the physical and mechanical properties of paper were studied using an analysis of variance. Refining changed the fibre surface, thereby promoting mechanical adhesion. PD temperature softened the fibres and changed their surface chemistry, while PD pressure improved the contact area between fibres. These changes led to an important improvement in IBS which explained, to a large extent, the variations in paper properties. Compared to air-dried paper, PD paper showed much higher properties for most tested pulps at all refining levels. These results were due to the increase in bonded areas. PD at 175°C substantially improved the wet tensile strength of paper due to the flow of lignin on the fibre surface, which protects the hydrogen bonds from moisture.

Keywords: press-drying, paper properties, internal bond strength, fibre properties, surface chemistry

1. Introduction

Fibre morphology, strength and adhesion are the main factors controlling paper strength [1–12]. Chemical composition is closely related to fibre strength and is an important factor in paper strength development [3, 5]. Among paper strength properties, tensile strength and tearing resistance are the most studied properties due to their importance during conversion and in end-use [1–12]. **Table 1** summarises the impact of the different fundamental fibre properties on paper tear, tensile and burst strength.

Properties	Morphological [1, 7–14]				Chemical [5, 15–22]			Mechanical [1–7, 15, 23–32]		
Strength Properties	**Length**	**Wall thickness**	**Coarseness**	**Microfibril angle**	**Cellulose**	**Lignin**	**Hemicelluloses**	**Strength**	**Flexibility**	**Adhesion**
Tear strength	+	–	–	–	+	–	+	+/–	–	+
Burst strength	+	–	–	–	+	–	+	+	+	+
Tensile strength	+	–	–	–	+	–	+	+	+	+

Table 1. Effect of increasing fundamental fibre properties on the development of the strength properties of paper.

The variation in tearing resistance is complex and researchers have carried out an impressive number of studies to understand this variation [2, 3, 5–8, 10]. Fibre length, strength and bonding are the main controlling factors. Although no clear relationship has been reported between tear index and fibre coarseness, in well-bonded sheets the tear index has been found to be higher in sheets with coarser fibres [6, 7].

Fibre length is an important factor in tearing resistance. Longer fibres improve tearing resistance, particularly for weakly bonded sheets [3, 6–8, 10–13]. However, fibre length is less important in well-bonded sheets having strong interfibre adhesion since sheet failure caused by tear is then controlled by the strength of the fibres [6, 7]. The tearing resistance is proportional to the square of fibre strength when fibre strength is modified without affecting other fibre properties or sheet structure [6, 7]. However, this does not necessarily imply that fibre failure is the prevailing mechanism of energy dissipation [8]. The elastic energy released when fibres or bonds fail depends on the load within the fibres and on the number of failures. All these entities are related to fibre strength.

The variation in the tensile strength of paper is controlled mainly by the internal bond strength. Indeed, several studies have reported clear positive linear relationships between the tensile strength and the internal bond strength [4, 25–27]. Fibre strength, morphology and coarseness are also important for the tensile strength development of paper. For example, the Page Equation [1] predicts the tensile strength from fibre properties including length, strength coarseness, fibre transverse perimeter, bond area and bond strength. This equation is widely recognised for predicting the tensile strength of paper. Clark [3] developed a statistical model to predict all paper properties from fibre properties. These models indicate the importance of the fibre properties for the development of paper strength.

The extent of fibre-to-fibre bonding is also important in determining paper strength. Improving this property is known to have beneficial effects on most sheet strength properties, except for tearing resistance. For the latter, the relationship is complex since it varies with the degree of interfibre bonding. **Figure 1** illustrates the general model that describes the variation of tear strength with the internal bond strength of paper. In poorly bonded sheets, increasing bonding strength improves the tearing resistance. However, in well-bonded sheets, higher bonding strength reduces the tearing resistance [3, 6–8]. This variation makes developing a model to predict the tear index from fibre properties difficult. Some attempts were made in the past to characterize this relationship using several approaches [7]. In general, fibre dimensions and physical properties are varied by either pulping different woods or fractioning a pulp. The paper properties from these pulps are generally modified by beating. The dependence of paper properties on fibre properties is then studied by statistical methods. This approach led to some good correlations, but there were no clear relationships because fibre properties are modified by beating and are generally interdependent.

The abovementioned studies have led to an excellent understanding of the tear mechanism and explained the role of each fibre property in the development of tearing resistance. For example, Page [6] elucidated the tear strength mechanism and determined the extent of its dependence on each fibre property by studying the effect on each property separately. Later, a model was developed [2] to describe the tearing energy of rupture of softwood pulps using

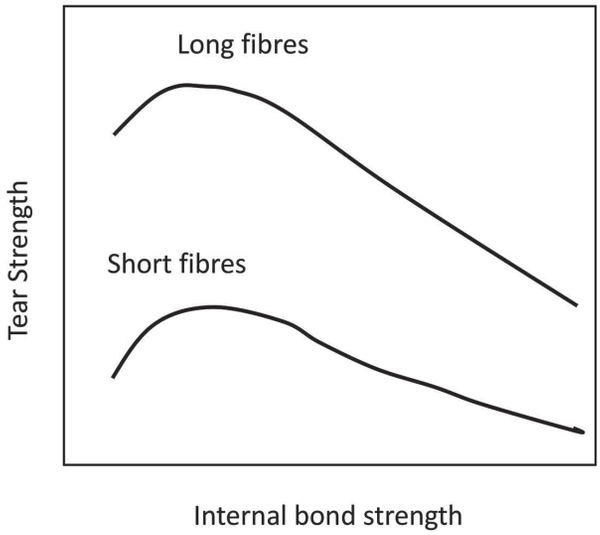

Figure 1. Typical model of variation of the tear index with fibre length and internal bond strength [6, 7].

the Page Equation [1]. However, most of these studies dealt with chemical pulps, particularly those made from softwoods. Only few studies dealt with the role of fundamental fibre properties of high-yield pulps [4, 12, 15, 28–30]. Moreover, few reports directly studied the effects of interfibre bonding [4, 15, 25–27, 30–32]. Generally, sheet density or light scattering coefficient or even tensile strength is used to depict changes in interfibre bonding.

There are few alternatives to improve the internal bond strength of paper. Chemical treatment and beating are the most used alternatives. Extensive literature exists on the impact of these alternatives on the strength development of paper. Press-drying is among the alternatives that can improve the paper properties especially internal bond strength due to improved compressibility by the combined action of pressure and temperature [30, 33–37]. In press-drying paper is dried under restraint through the application of pressure in the z-direction during the drying process while the paper is simultaneously in contact with a very hot drying surface, thereby leading to a web temperature in excess of 100°C [30, 33–37]. The important feature of this process is the fact that it takes advantage of the positive effects of high web temperature on both dewatering rate by reducing the viscous resistance of water and web consolidation by increasing the compressibility of fibrous material [34].

Several reviews are available on the physics of press-drying [33–38]. The main factors that control the mechanical properties of press-dried paper and the performance of this process are the mechanical pressure applied on the wet web, the moisture content in the web, the pressing time and the temperature [30, 33–37]. In addition to the improvement in drying rate, this process leads to substantial energy savings and improvement in paper properties [33–38]. This process has been commercialised as Condebelt drying [33, 38]. Despite the proven advantages to the Condebelt drying process, this technology is still not widely accepted in the pulp and paper industry [33, 38]. There are only two installations of this technology worldwide [33]. At an industrial level, Retulainen et al. [39] reported that the Condebelt drying process led to

substantial improvement in the paper properties and in the process efficiency as compared to the Cylinder drying process.

Despite the abundant literature on press-drying process and physics, only few studies have investigated the impact of process parameters on paper properties. Thus, laboratory pulp beating and paper press-drying experiments were conducted during this study on softwood and hardwood high-yield pulps so as to investigate the impact of this process while using large variations in fibre length, strength and interfibre bonding.

The main objective of this study was to discuss the impact of interfibre bonding development, intrinsic fibre strength and fibre length on the strength properties of press-dried paper. The specific objectives were: (1) to study the impact of pulp beating and press-drying temperature and pressure on paper internal bond strength; (2) to investigate the effect of IBS, intrinsic fibre strength and fibre length on paper strength development; and (3) to contribute to the fundamental understanding of strength development in press-dried paper.

2. Experimental procedures

Four high-yield pulps were used: one spruce TMP sampled after the first stage of refining from the Kruger, Trois-Rivières Mill (Quebec, Canada); three commercial bleached CTMPs obtained from the Tembec, Témisccamingue Mill, (Quebec, Canada) from birch, aspen and spruce. Pulps were beaten to various degrees in a PFI mill to ensure variation in fibre bonding (**Table 2**). The PFI mill was used to modify the cell wall structure and to minimise fibre fragmentation. Canadian standard freeness (CSF) was measured for each pulp. CTMP white spruce (*Picea glauca* (Moench) Voss samples were classified in a Bauer-McNett fibre classifier to investigate the impact of fibre length and distribution on strength development of paper. A total of nine pulps were obtained through the classification (**Table 2**) to ensure large variations in fibre length. The average fibre length of each class was measured by image analysis. The average weighted fibre length of each pulp was calculated on a dry weight basis (**Table 2**).

Series of 60 g/m^2 handsheets from each pulp were wet pressed and air-dried according to standard Tappi procedures and used as control samples. Other series were press dried at three different pressures (0.375; 0.750; 1.50 MPa) and temperatures (105; 140 and 175°C) using a hydraulic press with two heated platens. The moisture content (MC) of a sheet before press-drying is critical to the development of its strength [33–37]. In this study, handsheets had moisture contents (MC) ranging from 100–120% before press-drying. After press-drying, MC ranged from 6–9%. Paper properties were measured according to Tappi standard procedures. The internal bond strength was measured according to the method described in a previous report [25]. All samples were conditioned and tested at 20°C and 50% relative humidity (RH).

An analysis of variance was performed using the general linear model (GLM) SAS procedure [40] to test treatment effects. Regression and correlation analyses were performed with the CORR and REG SAS procedures. Results were considered significant at 95% and 99% probability levels.

Canadian standard freeness (CSF) (ml)	Fibre classification in a Bauer McNett (%)				Average fibre Length (mm)
	14	28	48	<48	
Unbleached Spruce TMP pulps (pulp sampled after the first stage of refining)					
475	22.4	34.5	12.8	31.3	1.43
295	13.7	28.9	20.4	37.0	1.40
220	12.5	28.5	20.5	37.5	1.35
130	12.8	27.5	20.2	39.5	1.32
Bleached Birch CTMP pulps (commercial pulp obtained from Tembec)					
420	0	9.9	50.5	39.6	1.03
340	0	19.0	39.7	41.1	1.02
250	0	18.2	36.8	44.6	0.96
200	0	15.5	36.5	48.0	0.92
Bleached Aspen CTMP pulps (commercial pulp obtained from Tembec)					
405	0	4.6	38.5	56.8	0.83
375	0	4.7	40.4	54.9	0.82
235	0	5.1	40.1	54.7	0.82
125	0	5.2	39.9	55.4	0.80
Bleached Spruce CTMP pulps (commercial pulp obtained from Tembec)					
750	100	0	0	0	2.85
750	0	100	0	0	2.03
750	0	0	100	0	1.34
750	40	40	20	0	2.07
540	32	32	16	20	1.88
540	24	24	12	40	1.78
480	16	16	8	60	1.22
450	8	8	4	80	0.98
480	0	0	0	100	0.66
540	28	31.5	15.7	24.8	1.75
485	29.8	27.7	15.9	26.6	1.74
400	29.8	27.2	16.9	26.1	1.74
350	29.7	27.5	13.5	29.1	1.70

Table 2. General characteristics of the studied pulps.

3. Results and discussion

3.1. Impact of pulp type, beating and press-drying on paper properties

Table 3 shows the results of the analysis of variance on the effect of pulp type, beating intensity and press-drying temperature and pressure on selected paper properties. All studied factors showed significant effects on paper properties, except for specific bond strength, where only pulp type had a significant effect.

The differences in the initial intrinsic characteristics of the studied pulps, including morphology, length distribution, intrinsic strength, specific area and chemical composition explain the significant effect of pulp type on paper properties. These differences are due to variations in wood species and pulping processes (**Table 2**). The first pulp is a commercial TMP spruce while the three other pulps are commercial CTMP pulps from birch, aspen and spruce. The chemical treatment softens the chips and results in longer, and more flexible pulps compared to the TMP pulp. The birch and the aspen CTMPs have shorter fibres than the spruce TMP and CTMP pulps. Compared to aspen, birch has higher wood density and higher cell thickness and fibre coarseness than aspen wood. All these differences along with the different fibre specific areas resulted in different paper properties (**Figures 2** and **3**).

The impact of beating on high-yield pulp properties is well-documented in the literature. Pulp beating modifies the fibre surface by generating fibrils, delamination and activation; improves the fibre specific area; slightly reduces the fibre length and produces fines [41, 42]. Data from **Table 2** show the changes in pulp properties. Fibre length shortened, and the proportion of fines increased, as the CSF decreased with beating intensity. All these changes improve the

Source of variation	DF	Paper properties					
		Density	ZSBK	IBS	SBS	BL	TI
Model	29	97.7**	11.1**	39.6**	n.s.	11.2**	9.5**
Pulp	3	897**	345**	358**	4.9*	322**	58.9**
Beating	2	33.2**	n.s.	24.7**	n.s.	29.3**	6.2*
Temperature	2	17.8**	n.s.	11.9**	n.s.	14.1**	31.2**
Pressure	2	14.7**	8.5*	6.0*	n.s.	4.0*	7.6*
R^2		0.98	0.94	0.94	0.28	0.94	0.77
CV, %		4.4	4.6	7.6	11.5	9.0	7.8

*Significant at $\alpha = 0.05$.

**Significant at $\alpha = 0.01$.

DF: Degree of freedom; ZSBL: Zero-span Breaking length; IBS: Internal bond strength; SBS: specific bond strength, BL: Breaking length; TI: Tear index; CV coefficient of variation; n.s. non-significant at $\alpha = 0.05$.

Table 3. Analysis of variance for the effect of beating and press-drying (temperature and pressure) on selected paper properties.

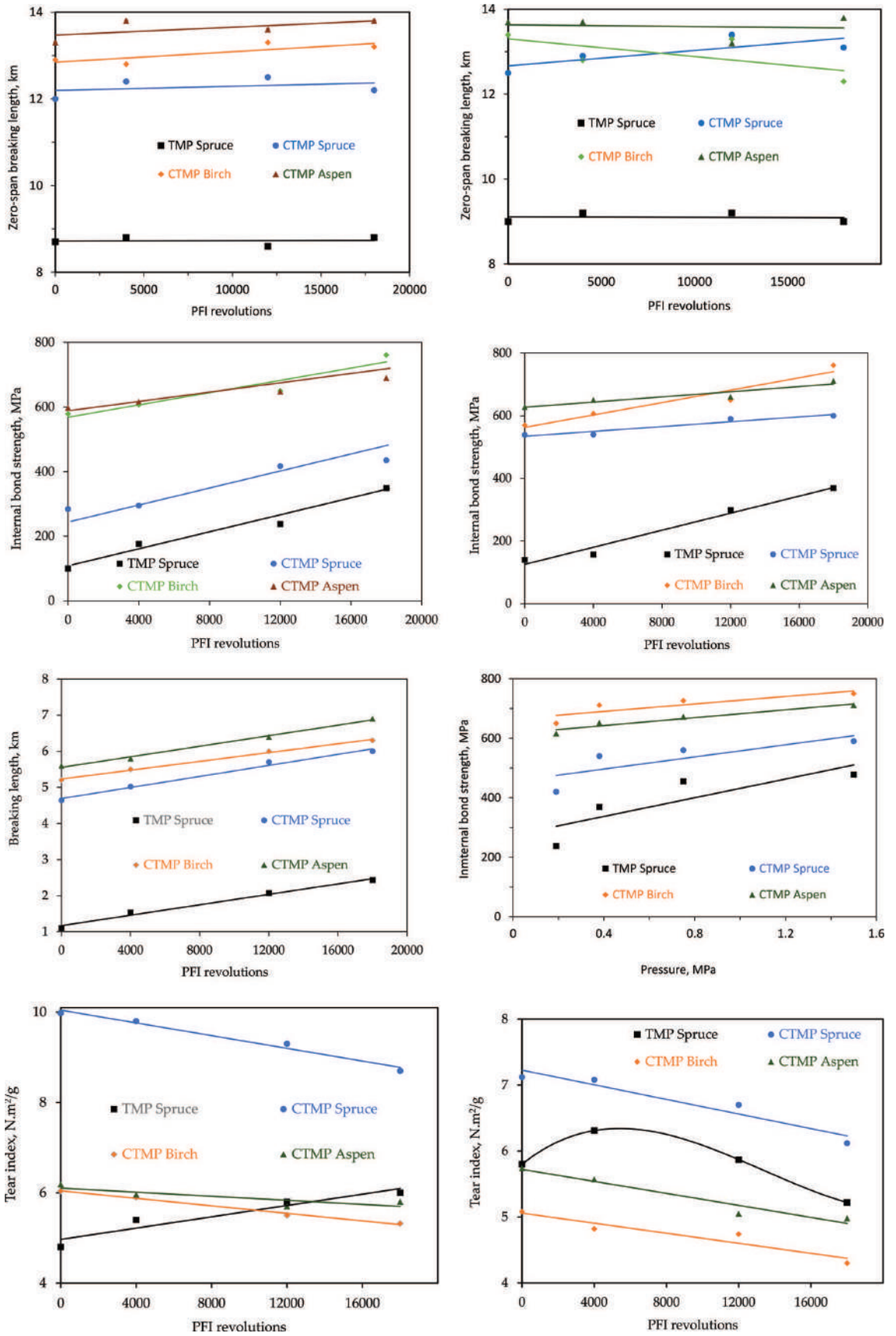

Figure 2. Effect of beating on selected properties of air-dried (left) and press-dried (right) paper made from high-yield pulps.

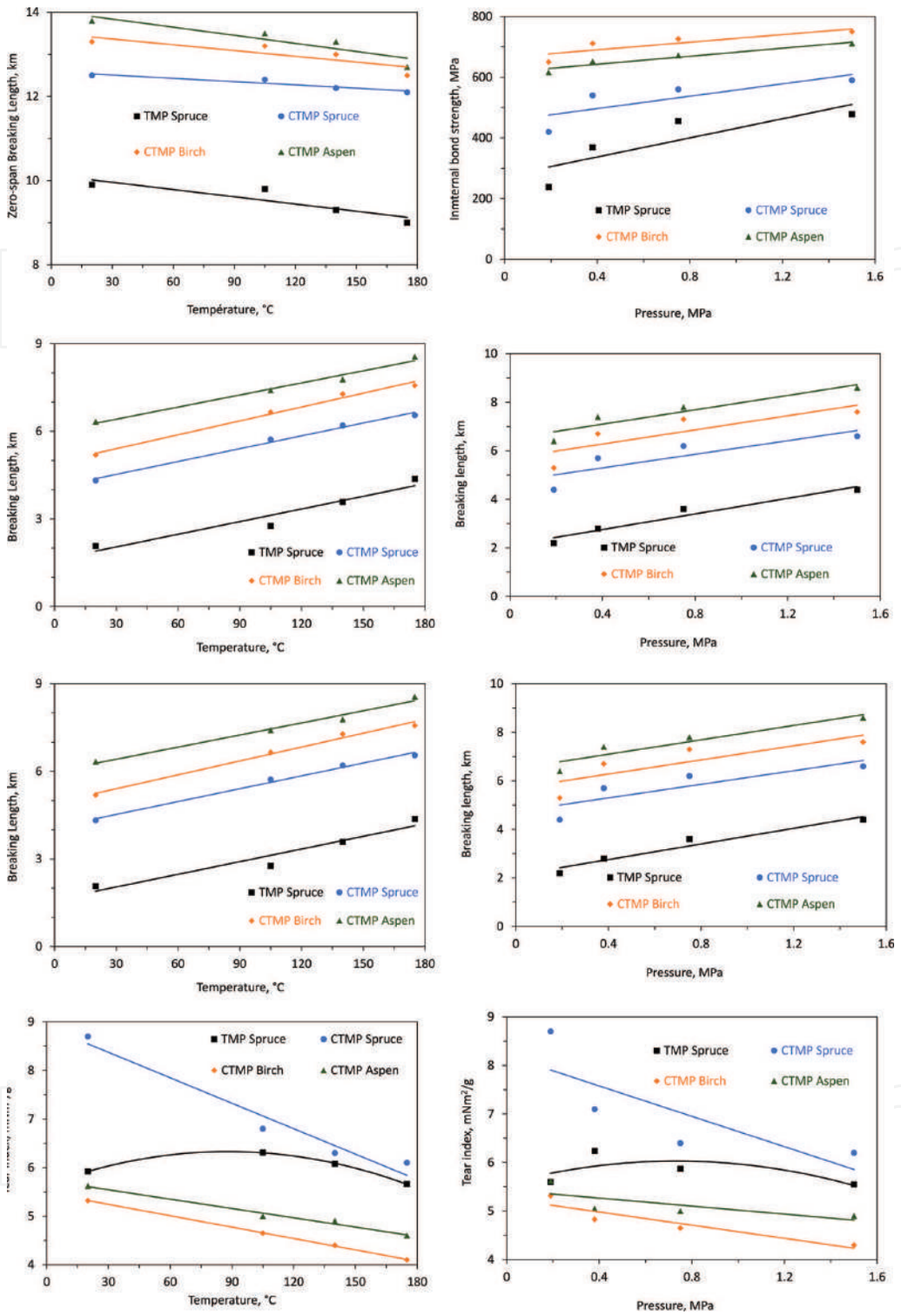

Figure 3. Effect of press-drying temperature (left) and pressure (right) on selected properties of papers made from high-yield pulps.

contact area between fibres, increase sheet density, lead to higher bonded areas and internal bond strength and consequently result in better tensile strength. **Figure 2** shows that beating improves the internal bond strength and the breaking length of both air-dried and press-dried paper from all high-yield pulps. However, beating decreases tear index, except for air-dried

paper from the spruce TMP, where this property increased with beating (**Figure 2**). This increase results from an improvement in bonding. The press-dried TMP showed an initial increase after a slight beating and then decreased linearly outwards. This initial increase is also due to the improved bonding. The following decrease occurs because, at higher beating levels, the paper is well-bonded and the tear mechanism is then controlled by the fibre strength [6, 7].

Despite the observed tendency of a slight increase with beating, the effect of this treatment on the zero-span breaking length for the press-dried paper was not statistically significant. This result could be explained by the large variation in this property among the studied high-yield pulps. The variation in this property due to beating is marginal compared to that caused by pulp type (**Figure 2**). At all beating levels and pulp types, press-dried paper showed slightly higher zero-span breaking length than the air-dried paper. This result may be explained by the fact that the press-dried paper is denser than air-dried paper. In the testing zone, press-dried paper has a higher area occupied by the fibre wall and less void.

Press-drying temperature showed a significant effect on all paper properties except for specific bond strength and intrinsic fibre strength (**Table 3**). **Figure 3** shows the variation of selected properties with press-drying temperature and pressure. Higher temperatures soften the wood fibres and make them more compressible. Thus, paper density increases with increased PD temperature, which leads to a higher contact area, and therefore, to a higher bond strength. This result was expected, and is in good agreement with previous findings where close and positive relationships were reported between the bonded area, the internal bond strength and the tensile strength of paper [4, 6, 7, 25–27, 30, 31].

The effect of beating and press-drying temperature and pressure on the specific bond of paper was not statistically significant (**Table 2**). At the tested beating and press-drying parameters, little variation of the specific bond strength is observed for spruce TMP (1600–1800 MPa), spruce CTMP (1400–1700 MPa), birch CTMP (1700–1900) and aspen CTMP (1500–1800). This result suggests that the improvement in the internal bond strength is attributed to the increase in the bonded area and not to a change in the nature of the fibre-to-fibre bonds. These are thought to be mainly hydrogen bonds that break easily under the action of water [15, 30, 43]. Zerhouni et al. [32] also concluded that press-drying temperature did not change the nature of fibre-to-fibre bond in papers made from CTMP, TMP and kraft pulps and sludge. The specific bond strength did not vary with neither the press-drying temperature nor the paper composition.

The variation in press-drying temperature also affects the fibre chemical structure as demonstrated in a previous report [15]. In this study, the surface chemistry of air-dried and press-dried spruce and birch CTMP papers were analysed by electron surface chemical analysis (ESCA) and the oxygen to carbon ratios (O/C) were reported. A decrease in the O/C ratio indicates an increase in the lignin content at the fibre surface. Results from this investigation showed that, at 105°C, only water and volatile matter were evaporated and no chemical change occurred on the fibre surface as the O/C ratio remained constant at 0.53 (**Table 4**). At 140°C, hemicelluloses start to degrade, but lignin and cellulose are not affected. However, the ESCA results did not show any notable change in the fibre surface at this press-drying temperature since the O/C ratio also remained constant at 0.53. A PD temperature of 175°C

	Birch CTMP				Spruce CTMP			
	25°C	**105°C**	**140°C**	**175°C**	**25°C**	**105°C**	**140 °C**	**175°C**
Carbon concentration, %	64.5	65.0	65.2	67.0	65.1	64.8	64.7	64.8
Oxygen concentration, %	34.6	34.4	33.8	32.2	34.5	34.1	34.5	32.4
O/C ratio	0.54	0.53	0.52	0.48	0.53	0.53	0.53	0.48
Wet breaking length, m	65	77	82	110	64	100	120	192

Table 4. Effect of drying temperature on the concentrations of carbon and oxygen, O/C ratio and wet breaking length of press-dried birch and spruce CTMP [15].

showed significant chemical changes at the fibre surface as indicated by the O/C ratio which decreased from 0.53 to 0.48. At this temperature, lignin flows at the fibre surface and protects the formed hydrogen bonds from moisture [15].

The variation in the wet breaking length of press-dried papers with temperature supports this finding (**Table 4**). For example, for the press-dried spruce TMP at 175°C, the wet breaking length improved by 364, 151 and 73% compared to those dried at 25, 105 and 140 °C, respectively. This improvement in the wet breaking length for press-dried CTMPs at 175°C was less important than that for the TMP. For the aspen, birch and spruce CTMPs, the improvement from 25–175°C was 136, 131 and 63%, respectively. The fact that the CTMPs were bleached led to less lignin present on the fibre surface, and these fibres were more hydrophile than the TMP fibres.

The PD pressure had a significant effect on all paper properties except for specific bond strength. Increasing pressure increases the bonded area, which improves the probability of hydrogen bond formation and also improves the density of the paper. This led to improved bond strength and consequently to improved tensile properties. The increase in the internal bond strength caused by pressure also led to a decrease in the tear resistance, as previously explained. Surprisingly, the press-drying pressure showed a significant effect on the zero-span breaking length (**Table 3**). Increasing the pressure decreased this property (**Figure 3**). The compression effect on the fibre increases the area occupied by the fibre wall in the testing zone, which is expected to improve the zero-span. However, a slight decrease in this property is observed with increasing press-drying pressure (**Figure 3**). This decrease could be attributed to the mechanical damage of the fibre due to increased pressure [5].

3.2. Impact of fibre strength on the development of paper properties

Intrinsic fibre strength plays an important role in the development of different paper properties. Indeed, rupture during testing could occur in the fibre or in the bond between fibres. Several studies [5, 26, 41, 44–51] demonstrated that during rupture in tensile testing of paper, some fibres pull out and others break. Beating weakens the fibres and the proportion of broken fibres during paper testing increases with the beating level.

There was no clear relationship between the tear index and the zero-span breaking length of the pulps at any of the beating levels tested. This is not because fibre strength did not influence

tear index, but because the effects of bonding and fibre length on tear index were more important and also because of the low range in fibre strength variation compared to those of internal bond strength and fibre length. Thus, the impact of fibre strength on the tear index could be hidden.

The relationship between zero-span breaking length and the tear index for beating levels where there was enough data with similar bond strength values was studied. Two distinct relationships were found at the same level of bonding, one for softwoods and one for hardwoods. These relationships were highly significant and explained more than 81% of the total variation in tear index (**Figure 4a**). This close relationship between the zero-span breaking length and tear index is in good agreement with previous findings [5–8, 51]. The difference between hardwood and softwood pulps is due to the impact of fibre length on the development of tear index.

For tensile strength, a linear relationship between breaking length and zero-breaking length was found for air-dried and press-dried paper (**Figure 4b**). This pattern of variation was expected, considering the variation in fibre strength among the TMP and CTMPs. Indeed, the TMP fibres showed lower fibre strength than the CTMP pulps at all beating levels and press-drying conditions. The press-dried paper tended to have slightly higher fibre strength and tensile properties compared to the air-dried paper. Better bonding can explain the higher tensile strength, while better fibre compressibility explains the better fibre strength of press-dried paper. The better fibre compressibility results in a higher area occupied by the fibre wall and lower void area in the test zone, which explains the higher zero-span breaking length of press-dried paper compared to air-dried paper.

Despite the high coefficients of determination ($R^2 > 0.85$), one can still observe a high scattering of the experimental data around the relationships for air-dried and press-dried papers. The variation in fibre morphology and bond strength, along with the experimental errors, explains this high scattering.

The close relationships between fibre strength and paper tensile and tear strengths are well documented in the literature [1–11, 26, 41, 44–51]. However, previous studies used chemical

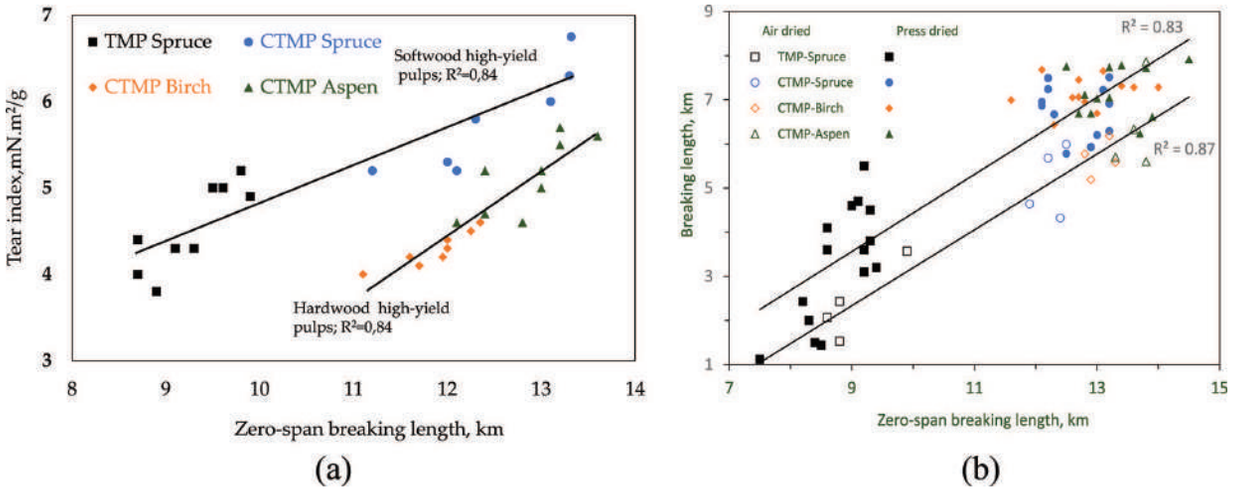

Figure 4. Effect of fibre strength on (a) the tear index and (b) the tensile breaking length of air-dried and press-dried papers made from high-yield pulps.

treatments or modification to vary the fibre strength to investigate this relationship [18–20, 49]. In addition, only a few studies investigated the impact of fibre strength on paper mechanical properties of high-yield pulps [12, 15, 28–30]. This study confirmed the importance of fibre strength in the development of tensile and tear strengths of high-yield pulps. Variations in pulp type, wood species and drying parameters along with refining led to an important variation in the fibre strength.

3.3. Impact of internal bond strength on paper properties

The observed variations in paper properties, namely the tear index (**Figure 5a**) and the breaking length (**Figure 5b**), are due to the effects of both beating and press-drying on internal bond strength. Data from the TMP and CTMP pulps followed two distinct relationships (**Figure 5a**). This result is due to several differences in the properties of TMP and CTMP pulps including fibre flexibility, compressibility and strength. Data from the present study show that the zero-span breaking length of the TMP ranged from 7.5 to 9.9 km while that of the CTMPs ranged from 11.7 to 14.7 (**Figures 2** and **3**). CTMP fibres are reported to be more flexible and more compressible than TMP fibres [29, 30]. The tensile modulus of elasticity of paper is closely related to fibre flexibility [9, 10, 30]. The tensile modulus of elasticity for the TMP papers ranged from 0.75 to 1.85 GPa while that of CTMP papers was much higher and ranged from 1.4 to 4.8 GPa [30]. Thus, CTMP fibres were more flexible than TMP fibres, thereby explaining the distinct relationships of TMP and CTMP paper (**Figure 5a**). As stated earlier, flexible fibres are more compressible and result in denser paper and in a higher area occupied by the fibre wall and a lower void area in the test zone.

For the TMP, the pattern of variation is typical of the tear index variation with interfibre bonding (**Figure 1**). The tear index initially increased with increasing bond strength to reach a maximum around 6 $N{\cdot}m^2/g$, beyond which it started to decrease consistently with increasing bond strength (**Figure 5a**). The initial increase is due to the fact that below the maximum tear index the paper is weakly bonded. Thus, more fibres pull out than break in the tear zone and the tear index is controlled to a greater extent by the number of bonds that break than by the fibre breakage. Beyond the maximum tear index, where the level of bonding is high, more fibres break than pull out along the tear zone [3, 6–8].

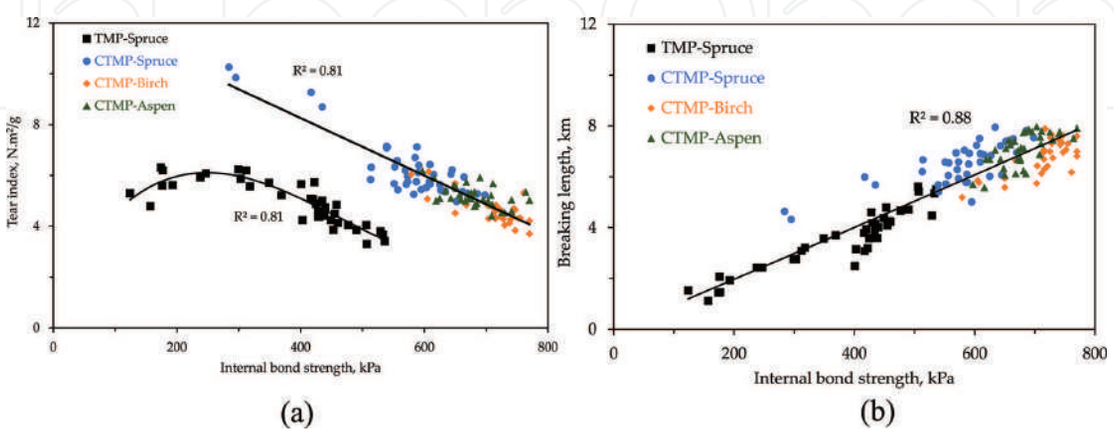

Figure 5. Effect of the internal bond strength on (a) the tear index and (b) tensile breaking length of press-dried and air-dried paper made from high-yield pulps.

In the case of CTMPs, the tear index of the pulps decreased consistently with increasing internal bond strength (**Figure 5a**). The three pulps tended to follow the same relationship. For each CTMP pulp, air-dried handsheets showed a higher tear index than press-dried ones (**Figures 2** and **3**). The experimental data of the internal bond strength and the tear index are scattered around both relationships (**Figure 5a**). This scattering is due to several factors including variations in fibre strength caused by beating and press-drying, to changes in fibre length due to species variation and to experimental error.

Fibre strength variation could also explain the differences between the tear index of various pulps. Despite its shorter fibre length, the aspen CTMP showed higher tear index values compared to the birch CTMP (**Figures 2** and **3**). The lower fibre coarseness and higher fibre strength of the aspen fibres compared to those of birch explain this result. The spruce CTMP showed the highest tear index because of its higher fibre length.

A close linear relationship was found between internal bond strength and tensile breaking length (**Figure 5b**). It is interesting to note that all the experimental data generated in the present study follow this relationship with a high coefficient of determination ($R^2 = 0.88$). This suggests that internal bond strength is the main controlling factor in the development of tensile strength of paper. This result is in good agreement with previous findings [4, 25, 41]. **Figure 5b** shows that the experimental data is scattered around the regression despite the high coefficient of determination. This scattering can be explained by the experimental error and the role of intrinsic fibre properties in the development of paper strength, namely fibre strength and fibre length.

3.4. Impact of fibre length and distribution on paper properties

Fibre length also plays an important role in the development of paper tearing resistance and tensile strength. The effect of fibre length is clearly seen in **Figure 4a** where the softwood pulps presented higher tear index values than the hardwood pulps at all constant fibre strengths. Similarly, the spruce CTMP showed a higher tear index than the birch and the aspen CTMPs (**Figure 4a**).

The tear index of both air-dried and press-dried paper was proportional to the fibre length of all classified spruce CTMP (**Figure 6a**). However, the tear index of press-dried handsheets was lower than that of air-dried ones. This result also shows that increasing bonding through press-drying decreases the tear index. The slope of the tear index variation with fibre length was also lower for the press-dried paper compared to air-dried paper. Thus, the dependence of tear index on fibre length was less important for press-dried paper. These results agree with Seth and Page [7] and can be explained by the tear mechanism as discussed in the previous sections. In the air-dried handsheets, the fibres were weakly bonded (internal bond strength varied from 80 to 290 kPa). Thus, tear index is controlled to a greater extent by the number of bonds that break along the length of the fibres. However, in press-dried handsheets, interfibre bonding was high (internal bond strength varied from 480 to 610 kPa), and consequently, the tear index is controlled to a greater extent by fibre breakage than by bond breakage.

Fibre length distribution also showed an important impact on the tear index (**Figure 6b**). An increasing proportion of fines led to a linear decrease in the tear index. In fact, higher proportions

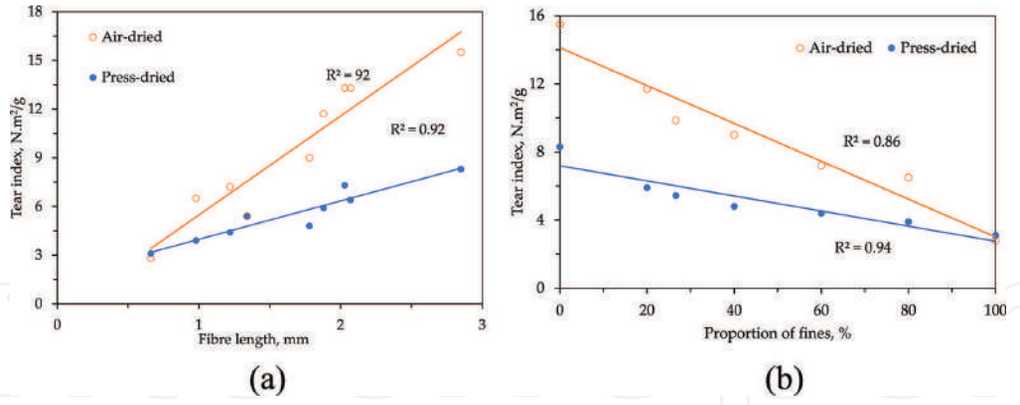

Figure 6. Effect of (a) fibre length and (b) distribution on the tear index of air-dried and press-dried paper at 175°C and 0.75 MPa made from white spruce classified CTMP pulps.

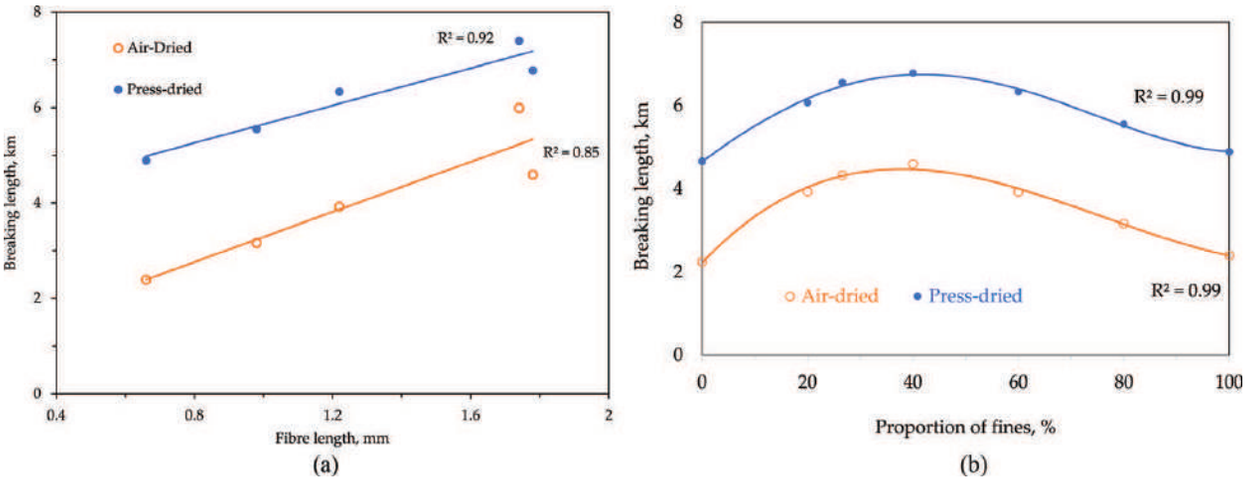

Figure 7. Effect of (a) fibre length (comparable CFS at 450 ± 30 ml) and (b) fibre distribution on the tensile breaking length of air-dried and press-dried paper at 175°C and 0.75 MPa made from white spruce classified CTMP.

of fines improved bonding and reduced the average fibre length in the paper. Both changes are known to decrease the tear index.

Figure 7a and **b** shows the impact of fibre length and distribution, respectively, on paper tensile strength. At comparable CSFs (450 ± 30 ml), an increasing fibre length led to a linear increase in the tensile breaking length. The latter is also controlled by the fibre distribution. The optimum breaking length occurred at around 40% of fines. The initial improvement in the tensile strength from 0% to about 40% is due to the improvement in fibre contact area. Beyond a 60% proportion of fines, the tensile strength showed a linear decrease due to the reduction in the proportion of long fibres. Long fibres lead to better stress distribution along the fibre network while fines lead to stress concentration in the fibre network [52], which explains the decrease in tensile strength when fines content is above 60%. The decrease in the tensile strength with high fines content is in a good agreement with previous findings [3, 11, 12, 41, 53].

4. Conclusion

The properties of high-yield pulps can be improved by beating and paper press-drying. Pulp refining changes the fibre surface morphology, promoting mechanical adhesion between fibres. Compared to air-dried paper, PD paper showed much higher internal bond strength, breaking length and wet breaking length for all tested pulps and at all refining levels. These results are due to the increase in the bonded areas. PD temperature softens the fibres and changes their surface chemistry, while PD pressure improves the contact area between fibres. These changes led to an important improvement in internal bond strength, which explained to a large extent the variations in the tensile strength properties of paper. Two opposite tendencies were observed for the tear index. In the well-bonded paper, press-drying leads to a lower tear index compared to air-drying, while in the weakly bonded paper, press-drying leads to a higher tear index compared to air-drying.

Fibre length and intrinsic strength also played important roles in the strength development of paper. However, their impact was less important for the press-dried paper as compared to the air-dried paper.

List of abbreviations

AD	air drying
BL	breaking length
CSF	Canadian standard freeness
CTMP	chemi-thermomechanical pulp
CV	coefficient of variation
DF	degree of freedom
ESCA	electron surface chemical analysis
IBS	internal bond strength
MC	moisture content
O/C	oxygen to carbon ratio
PD	press drying
RH	relative humidity
SBS	specific bond strength
TI	tear index
TMP	thermomechanical pulp
ZSBL	zero-span breaking length

Author details

Ahmed Koubaa[1]* and Zoltan Koran[2]

*Address all correspondence to: ahmed.koubaa@uqat.ca

1 Université du Québec en Abitibi-Témiscamingue, Rouyn-Noranda, Canada

2 Université du Québec à Trois-Rivières, Trois-Rivières, Canada

References

[1] Page DH. A theory for the tensile strength of paper. Tappi. 1969;**52**(4):674-681

[2] Page DH, MacLeod JM. Fiber strength and its impact on tear strength. Tappi. 1992;**75**(7):122-125

[3] Clark J'A. Components of the strength qualities of pulps. Tappi. 1973;**56**(7):122-125

[4] Andersson M, Mohlin U-B. Z-strength of mechanical pulps. Paperi Puu. 1980;**62** (10):583-586

[5] Wathén R. Studies on fiber strength and its effect on paper properties. [thesis]. Department of Forest Products Technology, Helsinki University of Technology; 2006

[6] Page DH. A note on the mechanism of tearing strength. Tappi. 1994;**77**(3):201-203

[7] Seth RS, Page DH. Fibre properties and tearing resistance. Tappi. 1988;**71**(2):103-107

[8] Kärenlampi PP. The effect of fibre properties on the tearing work of paper. Tappi. 1996;**79**(4):211-216

[9] Page DH, Seth RS, De Grace JH. The elastic modulus of paper. I. The controlling mechanisms. Tappi. 1979;**62**(9):99-102

[10] Cowan WF. Explaining handsheet tensile and tear in terms of fiber-quality numbers. Tappi. 1995;**46**(3):101-106

[11] Paavilainen L. Influence of fiber morphology and processing on the softwood sulphate pulp fibre and paper properties [thesis]. Helsinki: Helsinki University of technology; 1993

[12] Retulainen E, Luukko K, Fagerholm K, Pere J, Laine J, Paulapuro H. Papermaking quality of fines from different pulps – The effect of size, shape and chemical composition. Appita Journal. 2002;**55**:457-460

[13] Seth RS, Bennington CPJ. Fiber morphology and the response of pulps to medium-consistency fluidization. Tappi Journal. 1995;**78**(12):152-154

[14] Sundblad S. Predictions of pulp and paper properties based on fiber morphology [thesis]. Stockholm, Sweeden: KCH; 2015

[15] Koubaa A, Riedl B, Koran Z. Surface analysis of press dried-CTMP paper samples by electron spectroscopy for chemical analysis. Journal of Applied Polymer Science. 1996;**61**(3):545-552

[16] Oksanen T, Buchert J, Viikari L. The role of hemiocelluloses in the hornification of bleached Kraft pulps. Holzforschung. 1997;**51**(4):355-360

[17] Schönberg C, Oksanen T, Suurnäkki A, Kettunen H, Buchert J. The importance of xylan for the strength properties of spruce Kraft pulp fibres. Holzforschung. 2001;**55**(6):639-644

[18] Sjöberg J, Kleen M, Dahlman O, Agnemo R, Sundvall H. Fiber surface composition and its relations to papermaking properties of soda- anthraquinone and Kraft pulps. Nordic Pulp and Paper Research Journal. 2004;**19**(3):392-396

[19] Spiegelberg HL. The effect of hemicelluloses on the mechanical properties of individual pulp fibers. Tappi. 1966;**49**(9):388-396

[20] Treimanis A. Wood pulp fiber structure and chemical composition, their influence on technological processes. Nordic Pulp and Paper Research Journal. 1996;**11**(3):146-151

[21] Duchesne I, Hult E-L, Mohlin U, Daniel G, Iversen T, Lennholm H. The influence of hemicellulose on fibril aggregation of Kraft pulp fibres as revealed by FE-SEM and CP/MAS13C-NMR. Cellulose. 2001;**8**(2):103-111

[22] Lindström T. Chemical factors affecting the behaviour of fibres during papermaking. Nordic Pulp and Paper Research Journal. 1992;**7**(4):181-192

[23] Seth RS, Chan BK. Measuring fiber strength of papermaking pulps. Tappi. 1999;**82**(11):115-120

[24] Seth RS. Zero-span tensile strength of papermaking fibers. Paperi ja Puu – Paper and timber. Tappi. 2001;**83**(8):597-604

[25] Koubaa A, Koran Z. Measure of the internal bond strength of paper/board. Tappi. 1995;**78**(3):103-111

[26] Niskanen KJ, Alava MJ, Seppälä ET, Åström J. Fracture energy in fibre and bond failure. Journal of Pulp and Paper Science. 1999;**25**(5):167-169

[27] Forsström J, Torgnysdotter A, Wågberg L. Influence of fibre/fibre joint strength and fibre flexibility on the strength of papers from unbleached Kraft fibers. Nordic Pulp and Paper Research Journal. 2005;**20**(2):186-191

[28] Broderick G, Paris J, Valade JL, Wood J. Linking the fibre characteristics and handsheet properties of a high-yield pulp. Tappi. 1996;**79**(1):161-169

[29] Walker JCF. Pulp and paper manufacture. In: Primary Wood Processing: Principles and Practice. Dordrecht, The Netherlands: Springer; 2006. pp. 477-534

[30] Koubaa A. Amélioration de la résistance des liaisons dans le papier et le carton par raffinage et par pressage et séchage simultanés [thesis]. Université du Québec à Trois-Rivières

[31] Andersson M. Z-strength in pulp characterization – Chemical pulps. Svensk Papperstidning. 1981;**84**(3):R6-R14

[32] Zerhouni A, Mahmood T, Koubaa A. The use of paper mill biotreatment residue as furnish or as a bonding agent in the manufacture of fibre-based boards. J-For. 2012;**2**(2):19-24

[33] Lobosco V, Kaul V. An elastic/viscoplastic model of the fibre network stress in wet pressing. Part 2: Accounting for pulp properties and web temperature. Nordic Pulp and Paper Research Journal. 2001;**16**(4):313-318

[34] Lucisano MFC. On heat and paper: From hot pressing to impulse technology [thesis]. Stockholm: Royal Institute of Technology; 2002

[35] Andersson L, Back EL. The effect of temperature up to 90 C on dewatering of wet paper webs, evaluated in a press simulator. In: Proceedings of the TAPPI Engineering Conference. Atlanta, CA: TAPPI Press; 1981. pp. 311-323

[36] Back EL. A review of press drying. Technical Report D-224. STFI, Stockholm; 1984

[37] Back EL, Swenson R. The present state of press-drying of paper. In: The Role of Fundamental Research in Papermaking. Vol. Vol. 1. Cambridge: Mechanical Engineering Publishing Ltd; 1981. pp. 343-384

[38] Ghosh AK. Fundamentals of Paper Drying. In: Amimul Ahsan, editor Theory and Application from Industrial Perspective, Evaporation, Condensation and Heat transfer. InTech; 2011. pp. 535-582. ISBN: 978-953-307-583-9. Available from: http://www.intechopen.com/books/evaporation-condensation-and-heat-transfer/fundamentalsof-paper-drying-theory-and-application-from-industrial-perspective

[39] Retulainen E, Hämäläinen A. Three years of Condebelt drying at Stora Enso Pankakoski Mill in Finland. 1999 Tappi Engineering, Process & Product Quality Conference; 12-16 September 1999; Anaheim

[40] SAS Institute Inc. SAS Users Guide: Statistics. Version 6.03 edition. Cary: SAS Institute Inc; 1988

[41] Karlsson H. some aspects on strength properties in paper composed of different pulps [thesis]. Karlstad: Karlstad University; 2007

[42] Gharehkhani S, Sadeghinezhad E, Kazi SN, Yarmand H, Badarudin A, Safaei MR, Zubir MN. Basic effects of pulp refining on fiber properties—A review. Carbohydrate Polymers. 2015;**115**:785-803. DOI: 10.1016/j.carbpol.2014.08.047

[43] Przybysz P, Dubowik M, Kucner MA, Przybysz K, Przybysz Buzała K. Contribution of hydrogen bonds to paper strength properties. PLoS One. 2016;**11**(5):e0155809. DOI: 10.1371/journal.pone.0155809

[44] Van Den Akker JA, Lathrop AL, Voelker MH, Dearth LR. Importance of fiber strength to sheet strength. Tappi. 1958;**41**(8):416-425

[45] Buchanan JG, Washburn OV. The surface fractures of groundwood handsheets as observed with the scanning electron microscope. Pulp and Paper Magazine Canada. 1964;**65**(2):T52-T62

[46] Bronkhorst CA, Bennett KA. Chapter 7. Deformation and failure behavior of paper. In: Mark RE, Habeger Jr CC, Borch J, Lyne MB, editors. Handbook of Physical Testing of Paper. Vol. 1. 2nd ed. Revised and expanded. New York, Basel: Marcel Dekker Inc.; 2002. pp. 313-428

[47] Davidson RW. The weak link in paper dry strength. Tappi. 1972;**55**(4):567-573

[48] Kettunen H. Microscopic fracture in paper [thesis]. Espoo: Helsinki University of Technology; 2000

[49] Kärenlampi PYY. Fiber properties and paper fracture: Fiber length and fiber strength. In: Baker CF, editor. Transactions of the 11th Fundamental Research Symposium. The Fundamentals of Papermaking Materials. Vol. 1. Cambridge. UK: Pira International, September 21-26, 1997. pp. 521-545

[50] Yan N, Kortschot MT. Single fibre pull-out tests and the Elmendorf tear strength of paper. In: Proceedings 83rd Annual Meeting, Montreal. CPPA, Technical Section Preprints A. January 28-29, 1997; pp. A179-A183

[51] Lin B, He B, Liu Y, Ma L. Correlation analysis for Fiber characteristics and strength properties of softwood Kraft pulps from different stages of a bleaching fiber line. BioResources. 2014;**9**(3):5023-5033

[52] Migneault S, Koubaa A, Erchiqui F, Chaala A, Englund K, Wolcott MP. Application of micromechanical models to tensile properties of wood–plastic composites. Wood Science and Technology; 2011;**45**:521-532

[53] Fischer WJ, Mayr M, Spirk S, Reishofer D, Jagiello LA, Romana S, Colson J, Zankel A, Bauer W. Pulp fines—Characterization, sheet formation, and comparison to microfibrillated cellulose. Polymer. 2017;**9**:366-378. DOI: 10.3390/polym9080366

Chapter 5

The Value and Profitability of Converting Sawmill Wood By-Products to Paper Production and Energy Generation: The Case of Poland

Leszek Wanat, Elżbieta Mikołajczak and Jan Chudobiecki

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.80044

Abstract

Analyzing the relationship between production of wood-based products and the production of paper and its derivatives ever more often attention is paid to complementarity of the processes of production, recovery and recycling of key raw materials and finally to their value and profitability of production. In this context, two main trends in converting wood by-products are noticed: paper production and energy generation. Development of market of sawmill by-products constitutes a challenge for wood industry, which requires determination of the most efficient means of utilizing those by-products. One of the crucial criteria of making business decisions is the value of wood by-products. A method of valuation of those sawmill by-products when converted into briquettes, pellet, or energy was presented. This method allows for multilateral analysis of profitability of various means of utilizing wooden by-products, on the example of Poland. Based on comparative analysis, recommendations for wood-based industry were formulated.

Keywords: paper production, sawmill by-products, wooden pellet, wooden briquettes, energy, wood market, economic efficiency, Poland

1. Introduction

The competitive position of the Polish wood industry is relatively strong. It is an effect of the domestic forest resources, the quantity and quality of round timber acquired from the national resource base, as well as continually growing significance of wood-based products

in global production and trade. The total forest area in Poland amounts to 9.2 thousands hectares, which means the afforestation rate is 29.5% (0.24 ha of forest per capita). Public forests hold a domineering position (80.8%), mainly those managed by National Forest Holding "The State Forests" (77%), which is a natural monopolist on the wood market. Polish gross wood resources amount to approximately 2.5 billion m^3 of large timber (out of which almost 2.0 billion m^3 belongs to The State Forests). The position of forest and wood-based sector in Polish economy is determined by key factors: forests cover about 30% of Poland's territory, its share in GDP equals 2%, it creates workplaces and stimulates regional development. The contribution of forestry and wood-based sector to gross domestic product (GDP) in Poland amounts to: in case of forestry—0.3, and in case of wood industry—1.7%, which comes to an average share of forest and wood-based sector at the level of 2% (which is almost twice the world average) [1, 2]. Despite the imbalance in Polish wood- and wooden products market and the deficit of wood (a permanent phenomenon being an effect of the application of the principles of sustainable forest management), there is no threat for the development of wood-based industries in Poland [3, 4]. The following factors have a decisive impact on that: dynamic increase of demand for wood, wood being trendy and popular as an environmentally and human friendly raw material [5, 6]. A study of inter-sectoral cooperation seems justified with reference to the wood-based sector, especially owing to its territorial dispersion [7].

Polish wood industry plays an important role in the development of the national economy. The most important sectors based on wood include: sawmill industry, furniture industry, cellulose and paper industry, and market of wood-based panels. Coincidentally, it may be noticed that Polish market of wood by-products has developed dynamically. This industry is highly fragmented and focuses on small and medium-size businesses (with only a few large enterprises). A significant number of microenterprises (covering more than 30% of the entire sector) are not included in any official statistics. The share of wood-based industry in the production of the entire Polish processing industry is estimated at approximately 9%. Wood industry processes on average more than 38 million cubic meters of round timber per year, purchased mainly from National Forest Holding State Forests and worth more than 1.6 billion euro [8]. The potential of the wood sector is additionally confirmed by the level of employment—more than 260 thousand employees (including 125 thousand in furniture- and 50 thousand in paper industry). Value of production in wood-based sectors exceeds more than 20 billion euro (including 8 billion euro in paper industry and more than 7 billion euro in the furniture industry); here, the upward trend is maintained. The value of total export of wood industry products in Poland reaches more than 15 billion euro and there is a growing trend. Poland is the fourth largest exporter of furniture in the world (following China, Germany, and Italy), while other EU countries are the main recipients of Polish furniture [8]. Based on the case study of Poland, an attempt was made to evaluate the value and profitability of converting sawmill-wood by-products to paper production and energy generation. The aim of this study was to show a relatively easy method of verifying research hypothesis, which has assumed that the refining conversion of sawmill by-products, based on the example of selected new products processed in Poland enhances their value.

http://dx.doi.org/10.5772/intechopen.80044

2. Paper and paper industry in Poland and its economic significance

Despite domination of electronic economy and sometimes forecast marginalization of paper, it remains present in a modern society as one of the basic products of everyday use. Paper and paper industry still plays a significant role in creating economy of products based on wood. Contemporary knowledge allows us to state that paper which has been used for over 2000 years still successfully competes with electronic media, as well as the most modern multi-component packaging materials made of plastic, etc.

The areas of main functional utilization of paper and cardboard along with an attempt to identify the most important tendencies in its development were shown in **Table 1** [9]. In case of an increment, the enhancement was estimated. Based on own research the level of changes was measured (using a 5-grade scale: very high, high, medium, low, and neutral enhancement). Analyzing the main fields in the functional usage of paper and cardboard, the following key developmental trends were identified: Packaging and Specialty—a great variety (average

Paper functional use	Types of paper	Ready made products made of paper	Developmental trends
Information: - collection - distribution - storage	Newsprint; Coated and uncoated magazines (SC and LWC); Coated and uncoated woodfree printing and writing	Newspapers; Journals-Books; Computer printouts; Xerographic copies; Inserts; Illustrations	Increased use of multicolor printing and copying; Electronic media taking over banking/trading docs; Increased recycling as raw material and use of additives (high enhancement)
Packaging: - transportation - distribution - protection	Liner; Sack; Corrugating medium Folding box board; Liquid packaging board; Wrapping	Bags Boxes Wrappings Containers	Increased: use for distribution of food and composites; General increase in recycling of packaging materials; (average medium enhancement)
Hygienic: - personal care - cleanliness - disease prevention	Tissue - dry crepe - wet crepe	Toilet tissue; Kitchen towels; Facial tissue Napkins; Hand towels; Hospital clothing; Wipers	Use increases with general living standard; End of chain for recycling of fibers; Use of virgin fiber for top-end products (high enhancement)
Specialty—a great variety	Official papers; Filter paper; Fire resistant papers	Notes; Stamps; Air filters; Coffee filters; Baking paper	An ever-increasing number of new applications (average medium enhancement)
Multi-functionality	All papers	Packaging labels (source of information and form of advertising); Printouts on sanitary papers. Multi-functional packaging	Trend towards multi-functionality takes multiple usage of paper products: new model of product life cycle and the cycle of usage of goods made of paper (very high enhancement)

Source: Own elaboration based on [9].

Table 1. Main fields of functional use of paper and cardboard.

medium enhancement); Hygienic and Information (high enhancement), and above all Multi-functionality (which appears to be dominant). Leading identified developmental trend is the emphasis on multi-functionality of paper products (very high enhancement). This trend accounts for not only versatile, but also multiple usages of paper products. It therefore results in creating a new model of product life cycle and at the same time a new model of cycle of usage of commodities made of paper, which aims at an attempt to develop a closed cycle of production and utilization of paper.

3. Poland as a consumer of paper and cardboard

One of the determinants of level and quality of life and simultaneously competitiveness of regions is the volume of paper consumption per capita [10–19]. Annual average paper consumption in Poland amounts to 130 kg per person per year (**Figure 1**).

An upward trend is observed with a declining rate of increase (**Figure 2**). Between 1995 and 2015, the ratio of annual paper consumption increased more than three times. It is the biggest growth among all European countries included in the survey. Further increase in paper consumption in Poland may be expected, as an average for countries of Western Europe, to be

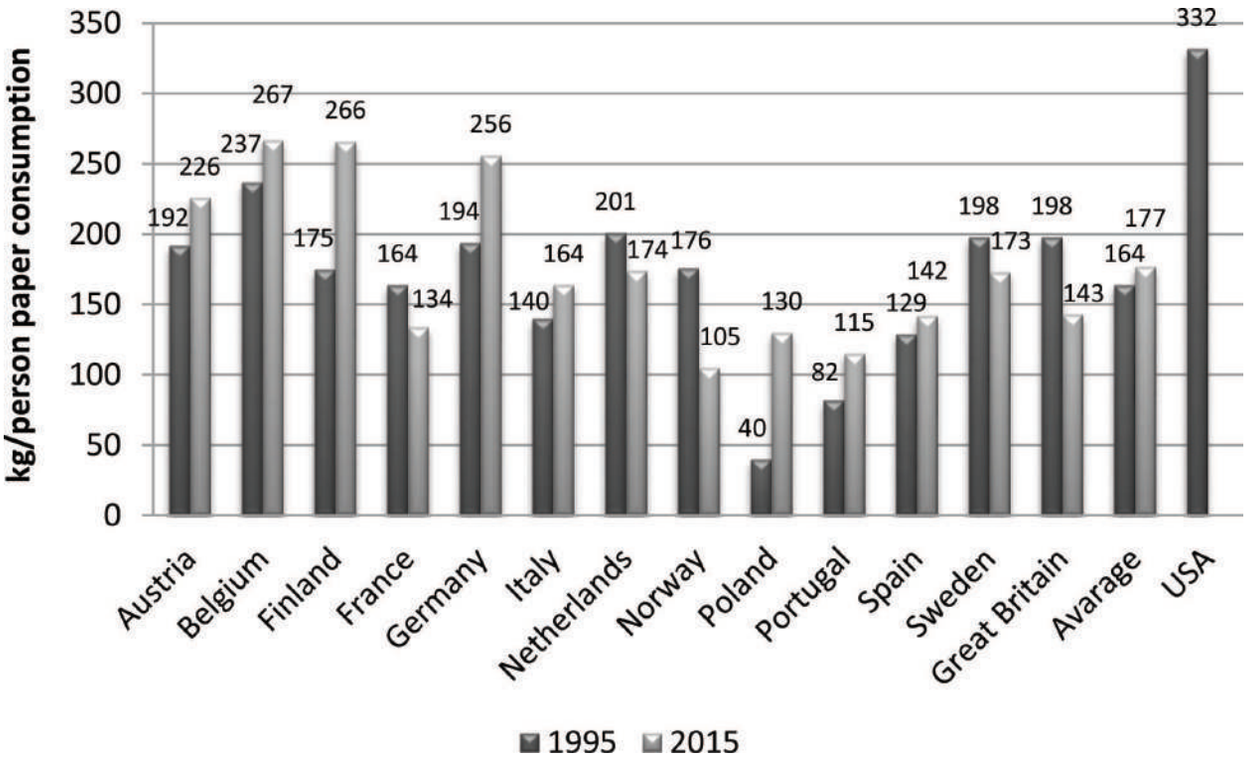

Figure 1. Comparison of paper and cardboard consumption in Poland and selected European countries in 1995 and 2015 [kg/person]. Legend: [X-axis label]: years 1995 and 2015; [Y-axis label]: kg/person paper consumption. Source: own elaboration based on [10, 11].

http://dx.doi.org/10.5772/intechopen.80044

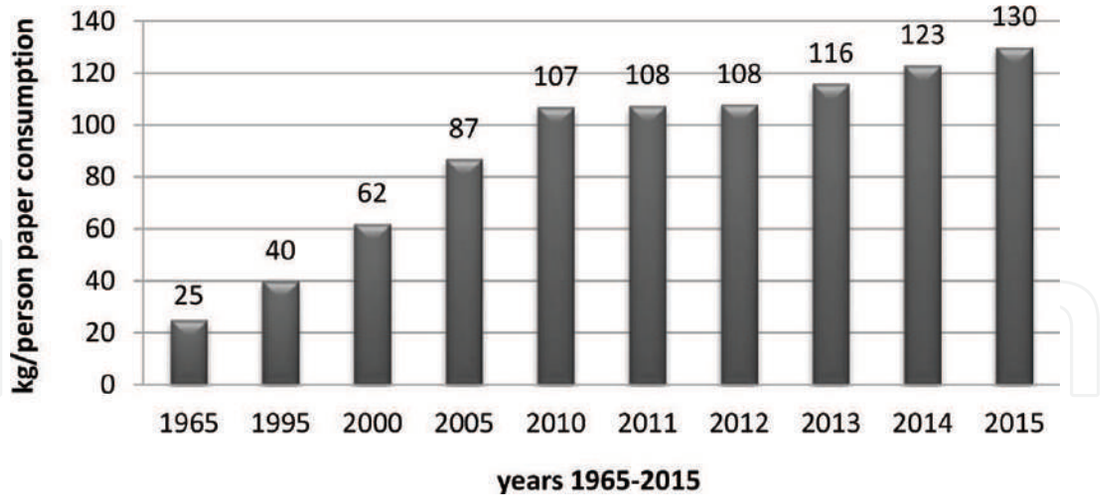

Figure 2. Paper consumption per capita in Poland [kg/person] in years 1965–2015. Legend: [X-axis label]: years 1965–2015; [Y-axis label]: kg/person paper consumption. Source: own elaboration based on [11–19].

177 kg per person. In some countries, the level of paper consumption is even two times higher than in Poland (Austria, Belgium, Spain, and Germany).

Even though a demand for newsprint decreases this trend is balanced by a growing demand for sanitary paper, packaging paper, and cardboard [20, 21].

4. Poland as a producer of paper and cardboard

Poland ranks eighth among CEPI member states as far as the production of paper and cardboard is concerned (the share of Poland is estimated at 5%) (**Figure 3**). Among the biggest paper industries or companies in Poland, there are [23]: Arctic Paper Kostrzyn SA GK with registered office in Poznan, Mondi Świecie SA GK in Świecie, International Paper-Kwidzyn sp. z o. o. in Kwidzyn, DS Smith Packing GK in Kielce, Polska Wytwórnia Papierów Wartościowych SA in Warsaw, and TFP sp. z o. o. in Kórnik.

In 2016, over 4.6 million tons of paper and cardboard was produced in Poland (**Table 2**), 5.6% more than in 2015. Transformation of Polish economy and direct foreign investments in paper industry led to 2.5 times increase in the volume of production, as compared to year 2000. Moreover, analyzing the dynamics of paper and cardboard production in Poland, one may indicate a steady upward trend in the period between 2006 and 2016 with a maximum reached in 2010 (13%) and high production ratios in 2009 and 2013 (over 7%).

According to product criteria, the most dynamically developing segment of production is the segment of paper hand towels made from paper pulp, paper, cellulose wadding, or webs of cellulose fibers. In the decade under analysis, there has been a steady increase in the production with a maximum in 2012 (30%) and short-term slump in 2013 (decrease by 5.8%).

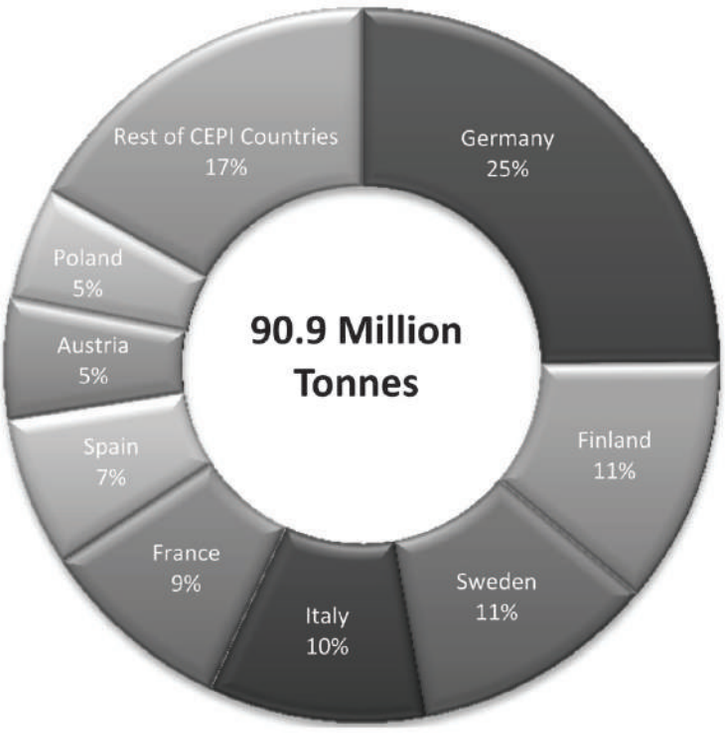

Figure 3. Major producers of paper and cardboard in Europe (2016). Source: own elaboration based on [22].

Production of corrugated cardboard increases from 3.3% in 2009 to 15.4% in 2011, subsequently reaching average values of 6% annually (2013–2016). Stable increase in the production is also observed in packaging segment including cartons, boxes, and cases made of paper and corrugated cardboard. An increase in the production of those commodities was noted from 4.5% in 2016 to 10.2% in 2012. The only decrease by 1.2%, took place in 2008.

Dynamic development of paper hand towels production as well as a steady increase in the production of cardboard and paper packaging compensates falls in the segment of newsprint in rolls or sheets.

Paper and paper-based products	**2000**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
	Units in thousands tons												
Soda or sulfate chemical woodpulp	751	802	825	814	820	826	881	894	848	881	881	873	877
Mechanical wood pulp*	244	249	345	353	331	319	299	307	304	306	301	286	303
Paper and paperboard/of which	1934	2732	2857	3005	3055	3275	3670	3756	3822	4106	4278	4399	4644
Newsprint	211	221	191	204	170	166	149	149	149	142	125	110	112
Graphic paper** and paperboard/of which	317	596	624	649	715	782	710	696	716	720	730	714	731
Graphic paper paperboard***	296	595	623	648	673	704	707	691	712	719	729	712	729
Uncoated, unbleached kraftliner	—	597	762	802	622	675	662	681	733	751	769	781	769
Semi-chemical fluting	—	136	189	180	185	280	178	188	178	180	178	154	170

http://dx.doi.org/10.5772/intechopen.80044

Paper and paper-based products	2000	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
	Units in thousands tons												
Uncoated Kraft paper and paperboard****	172	153	147	139	128	115	136	126	93	96	102	107	109
Corrugated paperboard	457	958	1054	1158	1210	1249	132	1528	1588	1703	1811	1933	2040
Sacks, bags of paper	83	90	104	117	102	126	124	126	115	113	121	124	131
Cartons, boxes of paper and corrugated paperboard	583	1155	1193	1417	1400	1523	1666	1747	1864	2010	2186	2408	2516
Toilet paper	116	215	208	219	237	259	255	268	297	298	304	330	367
Hand towels of paper pulp, paper, cellulose wadding, or webs	13	88	108	122	140	142	143	166	215	202	214	229	239

Source: own elaboration based on [24].
*Mechanical wood pulp; semi-chemical wood pulp; pulps of fibrous cellulosic material other than wood;
**Paper and paperboard of a kind used for writing, printing or other graphic purposes;
***Graphic paper and paperboard containing 10% and less by weight of the total fibers (by a mechanical process);
****Uncoated kraft paper and paperboard; sack kraft paper, creped or crinkled.

Table 2. Production of pulp and paper commodities in Poland (2000–2016).

This tendency is driven by competition from electronic media; however, one cannot explicitly state that this trend is sustainable. Within the period under the study, there has been production decline in this segment by more than 10%; however, in recent years, an increase was recorded (including that of 4.1% in 2016). The changes in the dynamics of production of

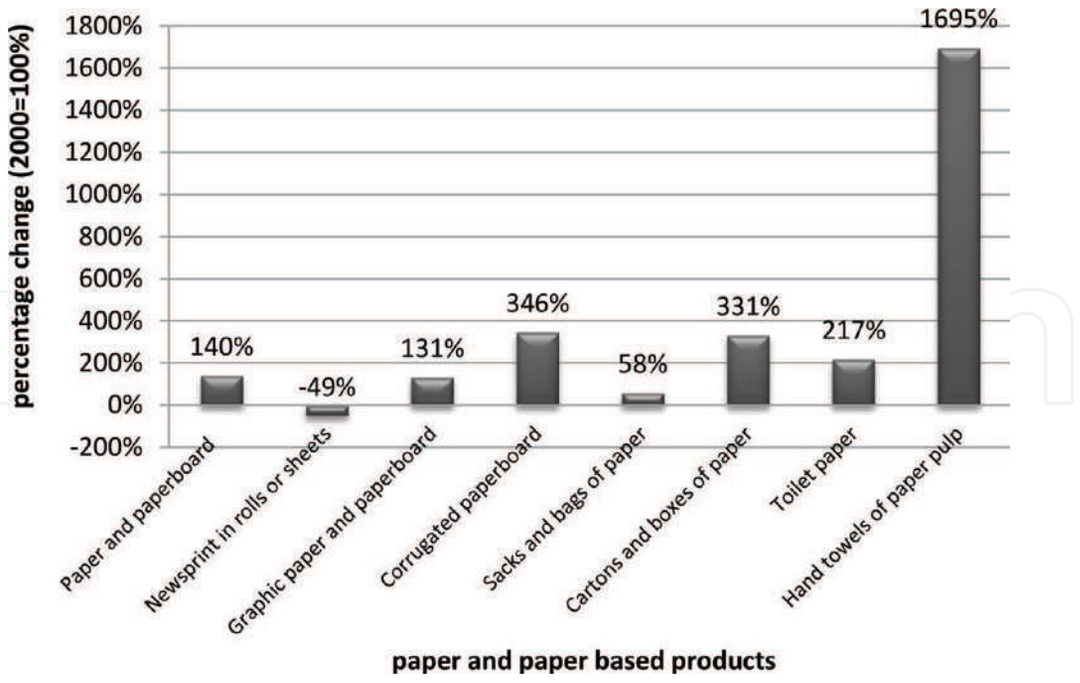

Figure 4. Dynamics of production of paper and cardboard and its different assortments in Poland in the period 2000–2016 (2000 = 100%). Legend: [X-axis label]: paper and paper-based products; [Y-axis label]: percentage change (2000 = 100%). Source: own elaboration based on [24].

individual paper, commodities were identified as a special example, which was also based on the carried out case study. It allows identifying the more important market trends with regards to products orientation. Analyzing changes in the total size of paper and cardboard production, as well as production broken down into the most important assortment groups in the period between 2000 and 2016 (**Figure 4**), the biggest growth (almost 18-times) was observed in the group of paper hand towels made of paper pulp, paper, cellulose wadding, or webs of cellulose fibers.

Also production of corrugated cardboard increased over four times, as well as the production of paper and corrugated cardboard packaging, such as cartons, boxes and cases. The smallest increase by "only" 60% was observed in the group of paper sacks and bags. While the production of newsprint in rolls or sheets dropped by almost 50%.

In a comprehensive approach as of year 2000 (that is within a period of 16 years, till year 2016), Poland recorded a total increase of 140% in the production of paper and cardboard.

5. The potential of Polish paper industry: international comparison

Presented results and conclusions were based on the data of Polish Main Statistical Office. Inclusion of international comparisons requires, at least within classification (assortment) used in Europe, adaptation of classification used by CEPI (**Table 3**). Structure by type of paper and cardboard production in CEPI member states (**Figure 5**) is dominated by graphic paper (39% share) as well as paper and corrugated cardboard (30% share).

In Poland, half of the production constitutes paper for corrugated cardboard production and the share of newsprint amounts to 20%, the next assortment group is sanitary papers with the share of 13% in the overall volume of paper industry production (**Figure 6**). The structure of Polish production is similar to the trends observed on paper and cardboard markets world-wide.

Analysis of CEPI statistics allows for a positive evaluation of the condition of European paper market, which in an analogical study period achieved better results than the USA or Canada [22]. In 2016, the total of 90.9 million tons of paper and cardboard was produced in Europe, which is a good result despite the 0.1% drop in overall production, as compared to year 2015. European market follows general trends of reducing weight of produced packaging materials, and most importantly focuses on efficient usage of resources [26]. In 2016, graphic papers production was limited (by 3.8%), and simultaneously there was an increase in the production of sanitary papers (by 1.1%) and packaging papers (by 2.4%). In the group of packaging papers, there has been an increase in the production of papers assigned for the production of corrugated cardboard (by 2.2%), used for manufacturing boxes (cartons) and other packaging used for transport purposes. Already, previously, indicated convergence of global trends with those observed on Polish paper and cardboard market, one may conclude that identification of economic tendencies for Polish case study concerning a selected Central and Eastern European country may be used as a source of forecast for the development of paper industry in other countries and the world regions.

http://dx.doi.org/10.5772/intechopen.80044

CEPI paper assortment group	CEPI Countries Production (P) and consumption (C)				Poland Production (P) and consumption (C)			
	2014		2015		2014		2015	
	P	C	P	C	P	C	P	C
	Unit in thousands of tons							
Newsprint	7594	7061	7042	6606	126	9.6	110	—
Uncoated mechanical	5634	4684	5503	4623	0	275	0	247
Coated mechanical	7050	5142	6789	4926	0	266	0	239
Uncoated woodfree	9017	7149	8934	7036	730	239	714	287
Coated woodfree	7364	4938	7020	4754	0	248	0	285
Total graphic papers	36,659	28,918	35,265	27,946	856	1039	824	1052
Sanitary and household	7001	6700	7153	6925	562	418	568	414
Case materials	26,205	24,870	27,059	25,894	2044	1981	2166	2205
Carton board	8551	5744	8710	5891	239	474	265	517
Wrappings	4106	2994	4071	2866	89	269	95	276
Other paper & board for packaging	4591	4159	4733	4300	90	166	96	177
Total packaging papers	43,452	37,767	44,572	38,951	2462	2890	2622	3174
Other paper & board	3910	3642	3881	3594	399	355	385	346
Total paper & board	91,019	77,028	90,872	77,416	4278	4701	4399	4986

Source: own elaboration based on [11, 25].

Table 3. Paper and Board Production and Consumption in 2014 and 2015 (CEPI).

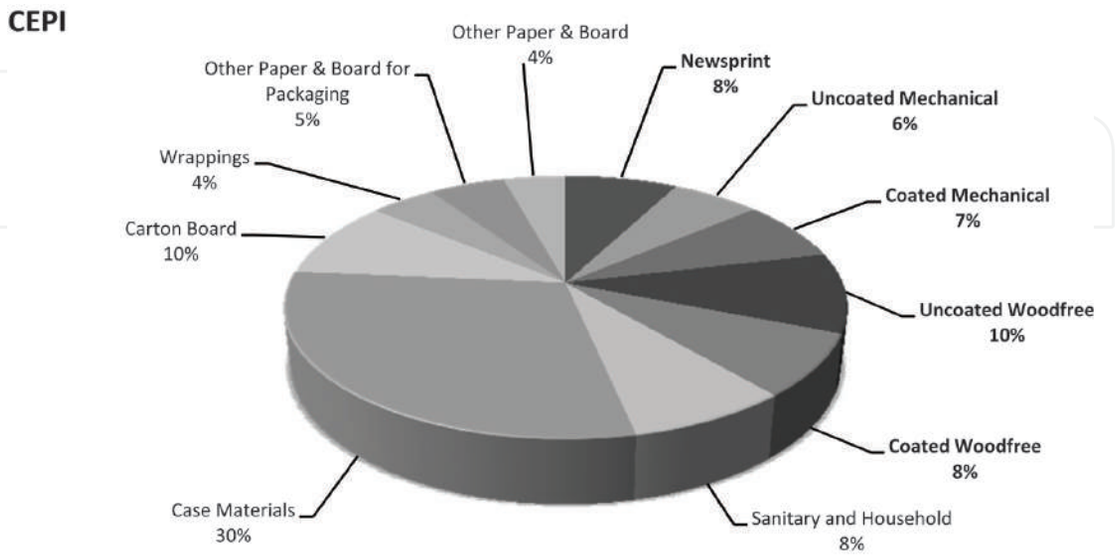

Figure 5. Structure of paper and paperboard production in CEPI countries in 2015. Source: own elaboration based on [11, 25].

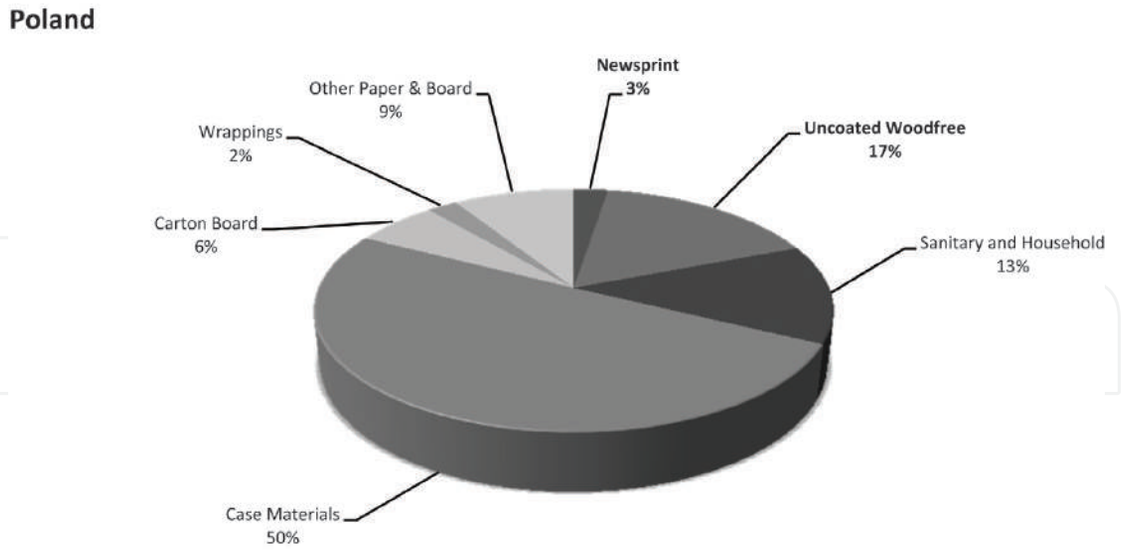

Figure 6. Structure of paper and paperboard production in Poland, in 2015 (CEPI). Source: own elaboration based on [11, 25].

6. Development prospects of paper and cardboard market

An attempt for identification of global development trends on the market of paper commodities based on a case study of local market (Poland), although seems to be a risky assumption, as reflected in the observations of consumers behaviors in Europe and world-wide. Those trends mainly concern two segments: paper and cardboard packaging (I) and sanitary papers (II). In the first case, development is determined by knowledge and belief of consumers regarding the endurance of packaging and the possibility of its recycling based on paper resources, while a growing demand for sanitary papers is determined by socio-economic factors related to the improvement in standard of living and demographic situation. China is a good example allowing us to draw conclusions that there is a link between growing GDP and an increase in the consumption of sanitary papers (**Figure 7**).

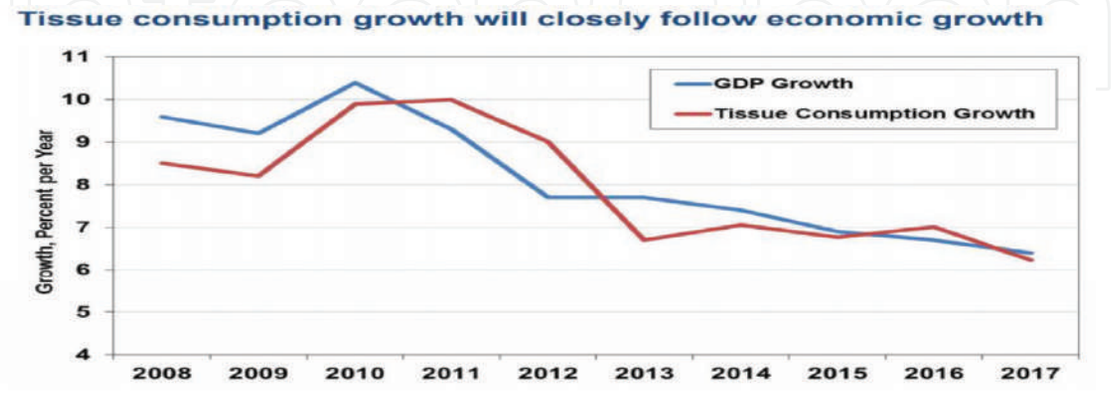

Figure 7. Comparison of GDP and tissue consumption changes in China (2008–2017). [X-axis label]: Years 2008–2017. Source: [27].

http://dx.doi.org/10.5772/intechopen.80044

This trend is stimulated by other complementary factors: urbanization, growth of net income, as well as consumer spending and primarily standard of living, natural element of which is access to high quality paper sanitary products. Moreover, even in the group of graphic papers, which is threatened by a decreasing demand due to a partial substitution by electronic media, a domineering position of new technologies over paper is not yet sealed.

Using descriptive approach, the following most important development trends of individual groups of paper products simultaneously reflect the formulated key trends in the development of the whole sector. Firstly, trends on the market of graphic papers were verified. Despite adverse opinions, the electronic media will not totally substitute paper as the medium of press, journalistic and scientific information as well as books and documents. Naturally, they will become a partial substitute facilitating and supplementing exchange of information on paper and communication. This investigation is supported by the following studies:

- The results of survey among office employees of 2400 small and medium-size enterprises from EMEA countries conducted on behalf of Epson Europe (2016–2017), which do not leave any doubts: pro-paper option dominates. 76% of respondents have an opinion that printing is a "very important" factor facilitating work and 75% states that "running paper-free office is unreal" (e.g., Poles print on average 29 pages a day) [28].
- 70% of Americans (including 69% aged 18–24) stated, in the survey conducted in September 2012 by Two Sides, that they prefer to read information printed on paper rather than displayed on a screen [29].
- Similar results were brought by research undertaken by Pew Research Center, which noticed that 6% of the respondents read books in digital format and 38% only in printed version. Hence, an imminent death of traditional books cannot be forecasted [30].
- Exchange-listed Association of German Book Sellers announced that in 2014, the existing buyers of electronic books ever more often read in printed formats (a drop in the number of e-book readers from 46% in 2013 to 33% in 2014) [31].
- A group of leading American companies removed advertisement promoting electronic invoices as more ecological. It has been justified by the statement that printing on paper has many unique features of environment protection (renewable resources), argument on rescuing forests is misconceived (more trees are planted than harvested), an actual cost of launching electronic documents is not known, while the majority still collects paper printouts of their e-documents for archive purposes [32].
- On the request of association of Consumers for Paper Options (CPO) in 2013, in the USA (and previously American post), it has been assessed that 80% of respondents are in the opinion that forcing clients to receive invoices (including those for energy consumption) only in electronic form is unacceptable [33].
- Scientists from McMaster University in Canada developed a method of printing on paper biosensors, which will be warning consumers against contaminated foods [34].

- At Bologna University, it has been proved that fruit sold on trays made of corrugated cardboard stay fresh for longer and are better protected than those sold on reusable plastic trays [35].
- Report "Paper and Productive Learning" [36] confirms domination of paper in academic education. 82% of students always or very often use paper when revising for exams, 74% uses paper for taking notes. Simultaneously, 64% of teachers are convinced that students better understand texts which are put on paper.
- Also, the study of artists' opinions revealed their conviction about greater efficiency of art expressed via paper than in digital format [37].
- Finally, association of German paper mills (*Verband Deutscher Papierfabriken* (VDP)) using research method of interview and observation of usability of paper in everyday life of Germans identified a significant role of paper in context of hygiene (80% respondents), transport (69%), and information (66%). Paper environmental safety was recognized and 79% of respondents were for invoices and documents delivered in paper format [38].

Meanwhile, economies worldwide record decreases in the production of graphic papers; however, stating its imminent decline or total elimination from usage would be unjustifiable. A totally reverse trend is observed on the market of paper packaging including corrugated cardboard packaging. Demand for this product grows in BRIC countries (Brazil, Russia, India, and China). Already, over 65% of packaging in Germany is manufactured from corrugated cardboard. This market in Europe is considered to be a growth pole (the pace of growth is estimated at 4.8% annually). Over half of British consumers (57%) prefer to pack their fresh food products in paper bags [39], and similar preferences are declared by 68% of European consumers [40]. Development of corrugated cardboard is also stimulated by new products manufactured based on cardboard, including: ULD pallet with honeycomb structure [41], corrugated cardboard bicycle helmets for self-service bike rentals [42], and KarTent, manufactured entirely from cardboard designed by a Dutch start-up [43]. In reaction to those trends, some factories producing graphic paper change their profile and launch production of corrugated cardboard: (a) Pro-Gest is reconstructing newsprint mill in Mantua, Italy, planning the production of corrugated cardboard in 2018 [44], (b) a similar investment takes place in Heinzel factory in Laakirchen in Austria [45], (c) a change of profile for corrugated cardboard will be launched in Madrid by International Paper, following their acquisition of newsprint paper from Holmen [46], (d) new investments are also carried out by LEIPA in Schwedt [47], Mondi (Slovakia)—production of "Kraft top white" [48], in Poland Stora Enso in Ostrołęka [49], Prinzhorn group (Eurobox Polska) [50], and Schumacher Packaging Group in Myszków [51].

European tissue paper market is growing at a quite stable pace, on average by 2–3% per year. A decline was recorded only in 2009. Western European markets record lower increase rate (up to 2%), while developing markets of Eastern Europe including Russia and Poland constituting 60% of the market record higher which increases (up to 4–5%) [52]. Tissue paper market is steadily developing (13% of Polish market of commodities made of paper in 2015) [53], and consumers are looking for goods in both economy and, ever more frequently, premium

http://dx.doi.org/10.5772/intechopen.80044

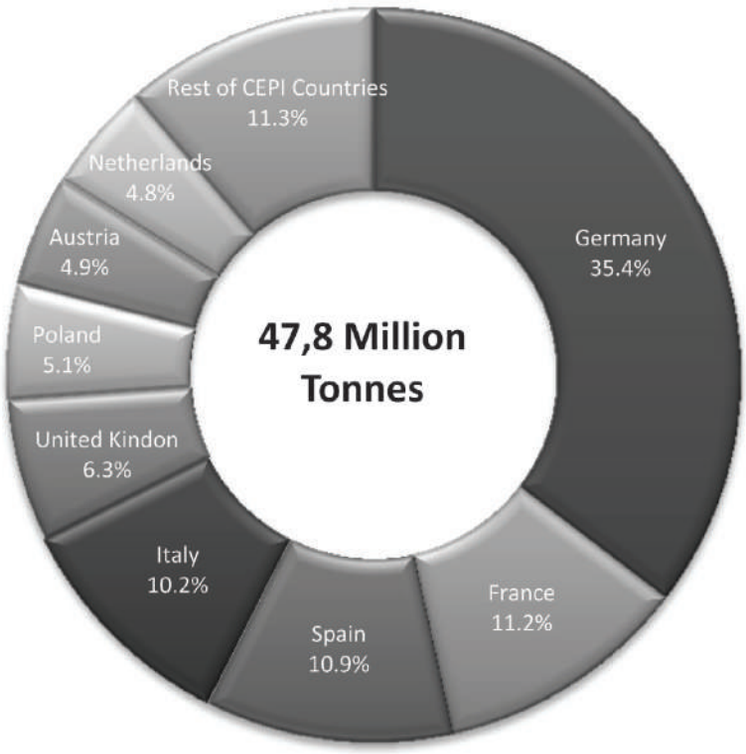

Figure 8. Use of recycled paper in CEPI countries in 2016. Source: own elaboration based on [25].

segment [54]. Along with the development of paper commodities market, one may also predict an increase in the usage of recycled paper. Currently this level is relatively stable with a slight growth in 2016 and amounts to 47.8 million tons (**Figure 8**). Collection of paper for recycling grew by 1% reaching the level of 56.4 million tons. Simultaneously, export of recycled paper increased by 5.6%, most of which was sent to Asian markets (91.7%). Level of recycling in EU countries, Switzerland, and Norway reached to 72.5% (increase by 0.7%).

Despite the fact that paper sector has to fight myths, such as "paper production destroys forests and environment," market of paper commodities is well perceived by consumers and will be developing. This development will include mainly those segments which are based on wood, and maximize the added value by trying to implement the principle of "zero waste." It is therefore about the type of industry which facilitates multiple recycling and converts into energy only, the materials which cannot be reused.

7. The value of sawmill wood by-products

In Poland, the use of sawmill by-products, which share in the total supply of all industrial wooden by-products (including veneer sector) amounts to 60%, becomes even more significant [55]. The aim of this analysis was to show a method of verifying research hypothesis, which has assumed that the refining conversion of sawmill by-products, based on the example

of selected new products processed in Poland enhances their value. The research used the data related to the prices of sawmill by-products, which was obtained via questionnaire and in-depth interview carried out at sawmills in Poland in 2015. Sawmills were selected using nonrandom sampling technique, in accordance with the minimum size of the sampling and the verification of statistical correctness of selection [56]. Evaluation of the profitability of processing the sawmill by-products into bio-fuels and energy was proposed based on:

1. Determining the value of sawmill by-products in the given areas of application
   a. Processing into bio-fuels [55]:

$$W_{pi} = \frac{1}{a_{pi}}\left[c_{jp}\left(1-\frac{m_j}{1-P}\right)-k_{pi}-k_{ti}\right] \qquad [\text{EUR/m}^3] \tag{1}$$

   b. Processing into energy [55]:

$$W_{ei} = c_{je}\,g\,\frac{19{,}5-2{,}5w_o}{1+w_o}\left(1-\frac{m_j}{1-P}\right)-k_{pi}-k_{ti} \qquad [\text{EUR/m}^3] \tag{2}$$

   where W_{pi} is the value of wooden residue being processed into any wooden fuel [EUR/m^3], I is the number of the type of by-product being converted, i ϵ <1, n>, P is the type of generated wooden fuel, p ϵ <1, n>, a_{pi} is the ratio of material intensity when processing the given by-product "i" into wooden fuel "p" [m^3/t, mp/t], c_{jp} is the unit sales price of the fuel "p" generated while processing by-products [EUR/t], m_j is the assumed net profit margin level m_j: {0.01; 0.05; … 0.15}, P is the Corporate Income Tax (CIT), in 2015 = 0.19, k_{pi} is the cost per unit of processing wooden residue [EUR/t], k_{ti} is the cost of transporting a unit of wooden residue [EUR/t], W_{ei} is the value of a given type of by-product of "i" number converted into energy [EUR/m^3], c_{je} is the unit price of selling energy generated from burning by-products [EUR/GJ], G is the bulk density of the type of by-product being burnt [t/m^3], and w_o is the absolute moisture of the by-product being burnt.

2. Comparing the determined value with the sales price of unprocessed sawmill by-products [55, 57]. Determined value of various types of sawmill by-products being processed into pellet, wooden briquettes, and energy was estimated and presented in **Table 4**, along with the sales prices of the post-production by-products from which they were processed.

The presented data indicate that a significantly higher increase in the value of sawmill by-products is reached by the entrepreneurs who process them at the place of their creation; hence, they do not bear any transport costs. The highest here is the value of post-production by-products processed into wooden briquettes, and slightly lower, in case of those being processed into pellet. The least profitable is processing "by-products" into energy, yet not for all types of by-products. The formula rationalizing the utilization of the stream of sawmill by-products via determining the value of their individual types which facilitates the selection

http://dx.doi.org/10.5772/intechopen.80044

Types of by-products		Sawmill by-product average price [EUR/m^3]	Value of by-products in conversion divided into								
			Pellet with margin			Briquettes with margin			Energy with margin		
			0.05	0.10	0.15	0.05	0.10	0.15	0.05	0.10	0.15
			Without transport cost [EUR/ m^3]								
			Including transport cost [EUR/ m^3]								
Sawdust	MSTR = 10%	28.10	46.48	39.89	35.68	49.52	45.54	41.56	29.21	**27.14**	**25.07**
			36.92	32.72	30.75*	42.35	38.37	34.40	**26.49**	**24.42**	**22.35**
	MSTR = 50%	24.12	39.67	33.52	29.59	42.65	38.94	35.23	33.85	31.46	29.06
			30.36	26.43	24.60*	35.57	31.86	28.14	31.51	29.11	26.72
De-fibered chips	MSTR =25%	28.10	44.93	39.96	34.99	52.62	47.87	43.13	33.60	31.22	28.84
			39.33	34.36	31.00**	47.02	42.27	37.52	31.75	29.37	**26.99**
	MSTR =50%	28.10	37.13	32.94	28.76	43.59	39.59	35.59	40.62	37.74	34.87
			31.51	29.59*	**23.14**	37.97	33.97	29.97	39.10	36.22	33.35
Pulp chips	MSTR =25%	35.36	50.25	44.93	39.61	57.05	52.01	46.97	**33.60**	**31.22**	**28.84**
			44.65	39.33	36.85*	51.44	46.40	41.36	**31.75**	**29.37**	**26.99**
	MSTR =50%	35.36	41.63	37.15	**32.67**	47.31	43.07	38.82	40.62	37.74	**34.87**
			36.01	**31.53**	**27.05**	41.69	37.45	**33.20**	39.10	36.22	**33.35**
Waste wood MSTR = 25%		24.59	52.68	46.75	40.82	61.88	56.22	50.55	33.60	31.22	28.84
			47.11	41.18	35.25	56.31	50.64	44.98	31.75	29.37	26.99

Source: own elaboration based on [55].
MSTR, moisture content; *, bb—sales only in big bag; **, bulk—only bulk sales. In **bold**, values of those converted by-products which came out as lower than the average sales price of sawmill wood by-products.

Table 4. Value of wood-sawmill by-products converted into pellet, briquettes and energy including and excluding cost of transport in Poland (2015).

of the most profitable one, from the sawmill perspective, and the way of utilizing its post-production by-products.

8. Criteria for evaluating profitability of processing sawmill wood by-products

Research attempts are taken to evaluate profitability criteria of converting the wooden by-products into wooden briquettes and pellets. Selected factors have been studied: namely threshold margin, maximum price (at which the raw material can be purchased for further

Type of wood by-product		Sawmill wood by-product average price [EUR/m^3]	Profitability of processing wood by-products generated as by-products and basic products						
			Break-even margin, m_{gr}		Maximum unit costs of conversion including transport	Maximum cost of transport per unit	Maximum distance from which raw materials can be transported*	Maximum purchase price of raw materials for conversion	Minimum selling price of finished product
			By-production	Basic production	$k_{pmax} + k_{tmax}$ [EUR/t],[EUR/m^3]*	k_{tmax} [EUR/t]	l [km]	c_{pub} [EUR/m^3]	c_{min} [EUR/t]
			Pellet						
			Briquettes						
Sawdust	MSTR 10%	28.10	23.76	15.23	88.33	44.37	232.89	40.80	122.83
			31.64	22.63	80.29	55.94	293.65	45.96	103.21
	MSTR 50%	24.12	22.12	13.09	94.11	41.31	204.97	34.44	126.82
			26.98	16.86	77.79	44.96	223.04	35.97	106.86
De-fibered Chips	MSTR 25%	28.10	21.86	16.22	91.82	38.13	254.76	44.18	112.98
			30.73	**24.82**	85.50	51.20	342.02	51.60	93.60
	MSTR 50%	28.10	15.52	9.88	82.27	27.06	151.54	36.30	124.05
			26.63	20.99	82.27	46.45	260.07	45.54	104.66
Pulp Chips	MSTR 25%	35.36	18.93	12.66	89.04	35.35	236.16	48.79	127.63
			26.41	19.79	81.00	46.69	311.95	55.24	108.24
	MSTR 50%	35.36	11.68	5.41	77.02	21.81	122.13	40.17	141.17
			18.75	12.13	68.98	33.16	185.65	45.57	121.78
Waste Wood MSTR = 25%		24.59	28.69	23.99	105.14	50.05	400.30	33.60	53.06
			37.34	**32.42**	98.81	61.70	493.48	31.75	60.98

Source: own elaboration.
MSTR, moisture content; *, transport 25 m^3, rate 1.06 EUR/km (**In bold** the highest values of: break-even margin level for various forms of utilizing sawmill-wood by-products); data presented excluding cost of transport.

Table 5. Profitability of processing wood by-products into pellets and briquettes and basic products in Poland (2015).

http://dx.doi.org/10.5772/intechopen.80044

processing), maximum unit cost of processing (including and excluding cost of transport), and the minimum acceptable by the producer sales price of the wooden biofuel (**Table 5**).[1]

Evaluation of profitability of processing sawmill by-products into ecological fuels and energy may be carried out in determining their value using the formula (3) [55], and then comparing it with the price of unprocessed "wooden residue." Transformation of the formula given below (Eq. (3)), which allows to set down the maximum possible margin, costs of processing, or the price level of the "residue" up to which purchasing of it will still be profit-making:

$$W_{pub} = \frac{1}{a}\left[c_j\left(1-\frac{m_j}{1-p}\right)-k_{jp}-k_{jt}\right] \qquad [\text{EUR/m}^3] \tag{3}$$

where W_{pub} is the value of wooden residue being processed into any wooden fuel [EUR/m^3], A is the amount of basic material necessary to generate one unit of a given wooden fuel [m^3/t, mp/t].[2] c_j is the sales price per unit of a given wooden fuel [EUR/t], m_j is the target net profit margin m_j: {0.01; 0.05; … 0.15}, P is the Corporate Income Tax (CIT), in 2015 = 0.19, k_{jp} is the cost per unit of processing wooden residue into a given wooden fuel [EUR/t], and k_{jt} is the cost of transporting a unit of wooden residue [EUR/t].

Comparative analysis used the data related to the prices of sawmill wood by-products, which was obtained via questionnaire carried out at wood processing plants (sawmills) in Poland in 2015. Analysis has embraced both companies (wood processing) which generated their own wood by-products as well as those which have to buy those (wooden) by-products (**Table 5**). Analysis of the juxtaposed values indicates that the most profitable form of processing wooden by-products is briquettes production and the highest margin level: 37.3% in case of the entrepreneurs who are in possession of those by-products may be obtained utilizing wood chips. The least profitable material for the production of briquettes is paper chips of 50% moisture content, due to their high price in the unprocessed form.

9. Conclusion

The formula rationalizing the utilization of the stream of sawmill by-products via determining the value of their individual types facilitates the selection of the most profitable, from the sawmill perspective, and the way of utilizing its post-production by-products. At the same time, it gives their owners the basis for choosing a versatile structure of their utilization. The above presented method may also be used when evaluating the profitability of production adopted as the main commercial activity by the entrepreneurs using the product available on the market.

---

[1] For comparison, the current average exchange rate is 1 EUR = 4.2705 PLN (Table No. 078/A/NBP/2017 of April 21, 2017; Source: http://www.nbp.pl/homen.aspx?f=/kursy/ratesa.html [Accessed: April 21, 2017]).

[2] The symbol "mp" means spatial meter in [mp/t] and [EUR/mp].

The following conclusions and recommendations were formulated:

1. The study showed that significantly higher increase in the value of further processed sawmill by-products is achieved by those entrepreneurs who process them at the place of their conversion without bearing any additional cost of transport.
2. Preferred and the most efficient way of utilizing wood by-products would be the sales of this raw material for further processing into paper and other derivatives (for example de-fibered chips), or alternatively direct utilization of solid pieces of wood assigned for a specific product which allows to gain added value, recycle, and reuse.
3. Only definite lack of resources primary usage should determine an optimum method of processing.
4. The highest value is characteristic for wooden by-products processed into briquettes, slightly lower for those processed into pellet. The least profitable is converting wooden by-products into energy.

   In detail, it was identified that:

   - The highest level of threshold margin is reached by the production of wooden briquettes utilizing wood chips (37.3%). The producer—who does not incur transport cost—may reach a higher margin, from 4.7% (wood chips) up to 9% (sawdust with 50% moisture content).
   - The maximum margin of net profit—determined for wooden pellet—is on average between 7.6 and 8% (including or excluding cost of transport) lower than in case of processing wooden by-products into briquettes.
   - Recommended for processing into pellet are: dry sawdust and paper chips—for which the average sales price may be higher.
   - The most profitable material—for briquettes production—constitutes de-fibered chips and wood chips (with moisture content of 25%), due to lower quality requirements concerning final product.
5. The descriptive analysis showed that significantly higher increase in the value of further processed sawmill by-products is achieved by those entrepreneurs who process them at the place of their conversion without bearing any additional cost of transport.
6. Investigating the further processed sawmill by-products (i.e. the wooden by-products into ecological fuels) is of essential importance for the economic development of regions, especially for industries characterized by high territorial fragmentation, e.g., the forest and wood-based sector in Poland.

   It needs to be highlighted that Polish wood market and derivative markets are determined by quasi-monopolistic organization of the market of wooden raw material. Institutional conditions of inter-municipal and inter-sectoral cooperation in Poland are concurrently an opportunity and a barrier for the establishment of partnerships with the participation of wood industry. Functioning of a secondary wood market, dispersed and territorially

http://dx.doi.org/10.5772/intechopen.80044

diversified, is a subject to market mechanisms. It creates a new market for sawmill wood by-products, which is an opportunity for the development of small- and microenterprises in the forest- and wood-based sector in Poland.

Author details

Leszek Wanat[1]*, Elżbieta Mikołajczak[1,2] and Jan Chudobiecki[1,2]

*Address all correspondence to: leszek.wanat@up.poznan.pl

1 Faculty of Social Sciences, Collegium Da Vinci in Poznan, Poland

2 Faculty of Economics and Social Sciences, Poznan University of Life Sciences, Poland

References

[1] Bergen V, Löwenstein W, Olschewski R. Forstökonomie. Volkswirtschaftliche Ansätze für eine vernünftige Umwelt- und Landnutzung. Vahl. Verlag: München; 2013

[2] Ratajczak E. Sektor leśno-drzewny w zielonej gospodarce. Poznań: ITD; 2013

[3] Wanat L, Lis W. Promotion of best practices-project proposal for the wood industry in Poland. Intercathedra. 2009;**25**:151-155

[4] Chudobiecki J, Wanat L. Industrial symbiosis and green business parks in the wood-based sector in Poland. In: Wood Processing and Furniture Manufacturing Challenges on the World Market. Zagreb, Croatia: WoodEMA; 2015. pp. 221-228

[5] Wanat L. Wood market science a new discipline of economic sciences supporting knowlege-based economy development. Intercathedra. 2009;**25**:149-151

[6] Kaputa V, Paluš H, Vlosky R. Barriers for wood processing companies to enter foreign markets: A case study in Slovakia. European Journal of Wood and Wood Products. 2016; **74**(1):109-122

[7] Chudobiecki J, Potkański T, Wanat L. Intermunicipal and inter-sectoral cooperation as a tool supporting local economic development. In: The Path Forward Wood Products: A Global Perspective. Zagreb: WoodEMA; 2016. pp. 187-196

[8] GUS Forestry (Leśnictwo) 2015. Warsaw, Poland: Main Statistical Office; 2015. [Internet]. July, 15, 2017. Available from: https://stat.gov.pl/files/gfx/portalinformacyjny/pl/defaultaktualnosci/5510/1/11/1/lesnictwo.pdf [Accessed: August 13, 2018]

[9] Ministry of the Environment. The finnish background report for the EC documentation of best available techniques for pulp and paper industry. Helsinki, Finland: EDITA Ltd.; 1997.

[Internet]. July, 15, 2017. Available from: https://julkaisut.valtioneuvosto.fi/bitstream/handle/10138/40277/SY_96.pdf?sequence=1 [Accessed: August 13, 2018]

[10] Woźniczko I. Papier—Zapotrzebowanie i produkcja. Przegląd Papierniczy. 1999;**7**:413-416

[11] Godlewska K, Jastrzębski M. Zużycie i produkcja papier u i tektury w Polsce w 2015 roku na tle krajów europejskich. Przegląd Papierniczy. 2016;**9**:593

[12] Cupryn J. Skup i wykorzystanie makulatury. Gospodarka Materiał. 1969;**9**:305-310

[13] Fornalski Z. Zużycie i produkcja papier u i tektury w Polsce w 2011 roku na tle krajów europejskich. Przegląd Papierniczy. 2012;**9**:547

[14] Fornalski Z. Zużycie i produkcja papier u i tektury w Polsce w 2012 roku na tle krajów europejskich. Przegląd Papierniczy. 2013;**9**:586

[15] Formalski Z. Zużycie i produkcja papier u i tektury w Polsce w 2013 roku na tle krajów europejskich. Przegląd Papierniczy. 2014;**9**:500

[16] Fornalski Z. Zużycie i produkcja papier u i tektury w Polsce w 2014 roku na tle krajów europejskich. Przegląd Papierniczy. 2015;**9**:485

[17] GUS (Central Statistical Office). Gospodarka Materiałowa w 1995 r. Warszawa: GUS; 1995

[18] GUS (Central Statistical Office). Gospodarka Materiałowa w 2000 r. Warszawa: GUS; 2001

[19] GUS (Central Statistical Office). Gospodarka Materiałowa w 2005 r. Warszawa: GUS; 2006

[20] Jastrzębski M. Rynek papierów higienicznych w Polsce. Przegląd Papierniczy. 2017;**3**:145

[21] Werner A. Krajowy rynek tektury falistej i opakowań. Przegląd Papierniczy. 2015;**2**

[22] European Paper Industry in 2016. [Internet]. July, 12, 2017. Available from: http://www.rynekpapierniczy.pl/artykul/europejski-przemysl-papierniczy-w-roku-2016-1191 [Accessed: August 26, 2017]

[23] Lista 500. Rzeczpospolita. April 29, 2016. [Internet]. July, 15, 2017. Available from: https://www.rp.pl/Lista-500/304289821-Lista-500–Rzeczpospolita-po-raz-18-prezentuje-zestawienie-czolowych-polskich-przedsiebiorstw.html [Accessed: August 13, 2018]

[24] GUS (Central Statistical Office). Production of industrial products in 2016. Warsaw, Poland: GUS; 2017

[25] CEPI Key Statistics 2015. European Pulp & Paper Industry. Confederation of European Paper Industries. Brussels: CEPI aisbl; 2016. [Internet]. July, 25, 2017. Available from: http://www.cepi.org/system/files/public/documents/publications/statistics/2016/FINALKeyStatistics2015web.pdf [Accessed: August 13, 2018]

[26] Tybuś J. Europejski rynek tektury falistej w 2016 r. Przegląd Papierniczy. 2017;**2**

[27] Uutella E. Global Tissue Business Outlook. RISI. [Internet]. 2015. Available from: http://www.cepi.org/system/files/public/documents/events/EuropeanPaperWeek2015/Uutela%20-%20RISI.pdf [Accessed: August 28, 2017]

[28] Papier nie Zniknie z Biur. Available from: http://www.chip.pl/2017/03/badania-mowia--jasno-papier-nie-zniknie-z-biur/ [Accessed: August 26, 2017]

[29] Anonymus. Amerykanie wolą czytać informacje drukowane. Przegląd Papierniczy. 2012;**3**:123

[30] Anonymus. Internet nie zabija czytelnictwa książek. Przegląd Papierniczy. 2016;**10**:589

[31] Anonymus. Powrót do książki drukowanej. Przegląd Papierniczy. 2014;**6**:293

[32] Anonymus. Początek końca antypapierowych reklam w USA. Przegląd Papierniczy. 2014; **4**:181

[33] Anonymus. Amerykanie za rachunkami papierowymi. Przegląd Papierniczy. 2015;**7**:354

[34] Anonymus. Papierowe wskaźniki patogenów. Przegląd Papierniczy. 2015;**7**:355

[35] Anonymus. Tacki z tektury falistej lepsze od plastikowych. Przegląd Papierniczy. 2016;**7**:399

[36] Paper and Productive Learning. The Paper and Packaging Board; 2016. [Internet]. July, 15, 2017. Available from: http://www.howlifeunfolds.com/app/uploads/2016/07/Paper_and_Productive_Learning_The_Second_Annual_Back-to-School_Report_2016.pdf [Accessed: August 13, 2018]

[37] Anonymus. Kreatywni cenią papier. Przegląd Papierniczy. 2016;**10**:589

[38] Anonymus. Papier wciąż nieodzowny. Przegląd Papierniczy. 2017;**4**:209

[39] Anonymus. Konsumenci preferują opakowania papierowe. Przegląd Papierniczy. 2015;**1**:2

[40] Anonymus. Konsumenci wolą papier do pakowania żywności. Przegląd Papierniczy. 2015;**5**:239

[41] Anonymus. Palety z tektury falistej do transportu lotniczego. Przegląd Papierniczy. 2017; **9**:518

[42] Anonymus. Kask rowerowy z tektury. Przegląd Papierniczy. 2017;**4**:212

[43] Anonymus. Tekturowy namiot nagrodzony. Przegląd Papierniczy. 2017;**6**:357

[44] Pro-Gest Orders Packaging Paper Machine for Mantua Mill [Internet]. 2017. Available from: http://www.euwid-paper.com/news/ [Accessed: August 26, 2017]

[45] Anonymus. Heinzel zainwestuje w Laakirchen Papier. Przegląd Papierniczy. 2016;**8**:454

[46] Anonymus. International Paper i papiery opakowaniowe. Przegląd Papierniczy. 2016;**3**:190

[47] Anonymus. Leipa przestawi papiernię w Schwedt na linery. Przegląd Papierniczy. 2016;**7**:401

[48] Anonymus. Mondi wybuduje linię papierów w Ružomberoku. Przegląd Papierniczy. 2016;**3**:13

[49] Anonymus. Stora Enzo w Ostrołęce. Przegląd Papierniczy. 2016;**5**:253

[50] Anonymus. Prinzhorn inwestuje w Sprembergu. Przegląd Papierniczy. 2016;**12**:723

[51] Anonymus. Schumacherg przejął Fabrykę Papieru Myszków. Przegląd Papierniczy. 2016; **12**:730

[52] Tybuś J. Rynek tissue na świecie. Przegląd Papierniczy. 2016;**2**:71-72

[53] Mrówczyński K. Rozwojowa branża wyrobów sanitarno-higienicznych z papieru. Chemia i Biznes. Rynek Kosmetyczny i Chemii Gospodarczej. 2016;**4**:14-16

[54] Gierasimiuk M. Papier w cenie. Przegląd Papierniczy. 2016;**2**:73

[55] Mikołajczak E. Ekonomiczne Aspekty Przerobu Odpadów Drzewnych na Paliwa Ekologiczne. Wydawnictwo Uniwersytetu Przyrodniczego w Poznaniu: Poznań; 2011

[56] Popek M, Wanat L. Price versus non-price factors of sector competitiveness: Case study of the round wood market in Poland. Intercathedra. 2014;**30**(2):71-77

[57] Mikołajczak E. Economic aspects of processing sawmill residue into briquettes. Intercathedra. 2013;**29**(3):64-70

Chapter 6

Environmentally Friendly Method for the Separation of Cellulose from Steam-Exploded Rice Straw and Its High-Value Applications

Guangjun Gou, Wei Wei, Man Jiang, Shengli Zhang, Tingju Lu, Xiaoli Xie, Fanbin Meng and Zuowan Zhou

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.79014

Abstract

Separation of cellulose from agricultural straw is one of the key bottlenecks hindering the application of such kind of biomass resources. In this chapter, we provide three environmental-friendly ways for separation of cellulose from agricultural straw pretreated with steam explosion, which include delignification with recyclable water-polar aprotic organic solvent, selective bio-degradation of the lignin component, and extraction of cellulose with imidazolium-based ionic liquids from the steam-exploded rice straw. The isolated rice straw celluloses have been adopted as an enhancement for all-cellulose composites (ACCs) and cellulose/cement composites. Ultra-high tensile strength (650.2 MPa) can be achieved for the ACCs containing the activated straw cellulose fiber (A-SCF). The cellulose/cement composites show a significant promotion in the flexural strength and fracture toughness. The new nonderivative solvent for cellulose, tetrabutylammonium hydroxide (TBAH) aqueous solution with urea as additives has been proved to be manipulable for dissolving cellulose.

Keywords: rice straw, steam explosion, cellulose, ionic liquids, all-cellulose composites, cellulose/cement composites, cellulose solvent

1. Introduction

Due to the ever-growing demand for energy, environmental impact caused by pollution, and the depletion of fossil fuel reserves, the demand for materials from renewable resources has

become an important matter [1, 2]. Lignocellulose biomass is considered one of replacing chemicals as well as fuels based on oil [3]. Agricultural residues is one of the most valuable and renewable lignocellulosic biomass as well as a promising alternative for cellulosic materials. Among different sources of agricultural residues, rice straw has been extensively investigated because it is one of the most consumed cereals in the world, about 650–975 million tons per year all over the world [4, 5]. Rice straw is composed of approximately 35% cellulose, 18% hemicellulose, and 15% lignin [6]. It can be used as raw material for conversion to high value-added products through chemical, biochemical and physical processes. However, cellulose is usually accompanied by other structural biopolymers, saying hemicellulose, and lignin. Therefore, determination of methods for the efficient separation of the constitutive biomass components has long been the major obstacles to its utilization.

Thus, novel environmental-friendly processes have been developed continuously, which include steam explosion [7], organosolv processing [8], the chlorine-free method [5], biological treatment [9], and ionic liquid isolation [10]. In this chapter, a brief review on the separation of rice straw cellulose in sustainable ways and the related utilization of the cellulose enhanced composites are systematically presented.

2. Steam explosion as pretreatment of rice straw

2.1. Introduction

Steam explosion (SE) has been a well-known technology for the pretreatment of straws during the separation of cellulose [11–13]. The critical process is the high-temperature hydrothermal treatment followed by a sudden exposure to atmospheric pressure [14].

During processing, the major hemicelluloses are partially hydrolyzed (autohydrolysis) due to high temperature transforming the acetyl groups connected with hemicellulose into acetic acid. Part of lignin can be depolymerized and leaving on the cellulose [15]. It is reported that the hydrolysis of hemicellulose separation was related to the reaction time and the pressure in the reactor [16]. For example, with the optimum condition (215°C, 7.5 min), a high-yield of sugar (81%) and ethanol (12.4%) can be obtained [17]. Therefore, the critical issue is a suitable condition of parameters, such as cooking time and the pressure, for efficient removal of hemicelluloses during the steam explosion which has been optimized by Zhou et al. [18]with a regression method in statistics.

2.2. Optimizing of conditions for steam explosion

Naturally dried rice straw was cut into pieces of about 2–3 cm in length and then shredded in a high-speed pulverizing mill. The crushing process was necessary for the effective infiltration of steam into the cell. The rice straw was then put into the reactor with a solid to liquid ratio of 3:1 (w/w). The high-temperature steam was poured in by opening a valve and cooked for a specified time, followed by explosion procedure.

http://dx.doi.org/10.5772/intechopen.79014

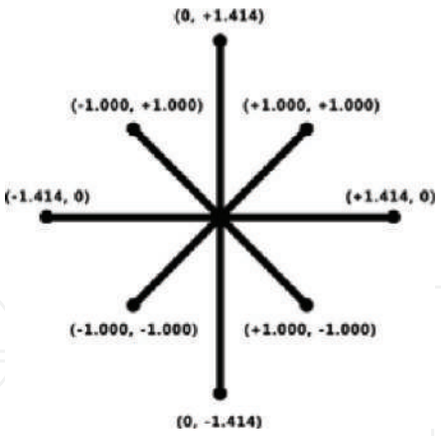

Figure 1. Spatial distribution of these two factors.

Normalized	Pressure *X1* (MPa)	Cooking time *X2* (min)
1.414	3.2	32
1.000	3.0	30
0.000	2.5	25
−1.000	2.0	20
−1.414	1.8	18

Table 1. Parameter table.

A series of experiments were designed to investigate the effects of pressure *X1* (corresponding to temperature) and cooking time *X2* on the final product of hemicelluloses (γ-Cellulose) and cellulose (α-Cellulose) in the process of steam explosion by using a regression method in statistics. The number of the experiments (N) meets the equation below:

$$N = 2^m + 2m + 3 \tag{1}$$

where, m is the number of independent factors and "3" is the number of experiments in the central point, which could improve the accuracy of the regression.

The spatial distribution of these two factors (*X1*, *X2*) in this regression design is illustrated in **Figure 1**. According to the earlier works of exploratory, the interval factors have been determined, as shown in **Table 1**.

The details of the experimental plan as well as the content of hemicelluloses and cellulose of the steam-exploded straw are shown in **Table 2**. The sample 11 of steam explosion in **Table 2** is selected for the comparison of the main components with the original rice straw. It is clear that most of the hemicelluloses can be hydrolyzed and extracted at the proper set of conditions for the steam explosion.

No.	*X1*	*X2*	Treatment severity lgR_o[a]	γ-C (%)[b]	α-C (%)[b]	DP[c]
Rice straw	—	—	—	17.98	35.06	1123
1	1.000	1.000	6.19	3.01	70.43	229.5
2	−1.000	1.000	5.60	8.66	69.85	303.3
3	1.000	−1.000	6.01	3.84	65.03	198.4
4	−1.000	−1.000	5.42	3.25	67.58	272.7
5	0	1.414	5.92	6.29	72.96	360.2
6	0	−1.414	5.67	6.68	70.51	276.2
7	1.414	0	6.25	2.72	61.77	246.0
8	−1.414	0	5.37	8.46	70.49	418.6
9	0	0	5.81	1.45	64.80	268.3
10	0	0	5.81	1.38	64.72	266.0
11	0	0	5.81	1.10	64.65	270.9

[a]Refers to the strength of the steam explosion and could be calculated by Eq. (2).

[b]The contents of α-Cellulose and γ-Cellulose, respectively, which are determined according to Tappi method T203 cm-99.

[c]The intrinsic viscosity of α-Cellulose ([η]) that is measured in cupriethylenediamine (CED) solution, and from which the DP (degrees of polymerization) could be calculated by the equation below, according to SCAN-CM 15:88 standard.

Table 2. Effect of reaction time and pressure on the final content of hemicelluloses and cellulose [18].

The value of lgRo is proportional to the strength of steam explosion. Additional hydrolysis of α-Cellulose may happen along with higher lgRo, as indicated by sample 7 in **Table 2**.

$$R_0 = \int_0^{t[min]} \exp\left(\frac{T[^\circ C] - 100}{14.75}\right) \bullet dt \tag{2}$$

$$DP^{0.76} = [\eta]/2.28 \tag{3}$$

Experimental data in **Table 2** have been fitted to the following second-order polynomial:

$$Y_i = a + bX_1 + cX_2 + dX_1^2 + eX_2^2 + fX_1X_2 \tag{4}$$

where Y_i refers to α-Cellulose, γ-Cellulose and SCAN viscosity, respectively. The symbols of *a*, *b*, *c*, *d*, *e* and *f* are the corresponding estimated parameters. Regression has been carried out using a nonlinear method with the SPSS software, and the result data are as shown in **Table 3**. R^2 values of α-Cellulose and γ-Cellulose are close to 0.9, which indicate good models for these factors. However, the model of SCAN viscosity is not well fitted, as indicated by the low value of the R^2.

Since the regression has established good models (Eqs. 5 and 6) describing the relationships between independent factors (referring to *X1* pressure and *X2* cooking time of the steam explosion process) and the responses (referring to Y_i, final content of γ-Cellulose and α-Cellulose).

Symbols	γ-Cellulose (%)	α-Cellulose (%)	SCAN viscosity
a	1.31	64.72	268.42
b	−1.65	−1.79	−48.76
c	0.50	1.34	26.80
d	1.80	0.54	14.93
e	2.25	3.28	4.85
f	−1.56	0.78	6.95
R^2	0.896	0.861	0.332

Table 3. Characteristic constants and R^2 of the regression [18].

These relationships can be visualized, as shown in **Figure 2**. The values of coordinates of their nadirs are given in **Table 5**.

$$Y_{\gamma\text{-C}} = 1.31 - 1.65 \times X_1 + 0.50 \times X_2 + 1.80 \times X_1^2 + 2.25 \times X_2^2 - 1.56 \times X_1 \times X_2 \quad (5)$$

$$Y_{\alpha\text{-C}} = 64.72 - 1.79 \times X_1 + 1.34 \times X_2 + 0.54 \times X_1^2 + 3.28 \times X_2^2 + 0.78 \times X_1 \times X_2 \quad (6)$$

As discussed earlier, the aims of the steam explosion maximizing the removal of the γ-Cellulose and the loss of α-Cellulose. From the observation, there is no serious contradiction between these two aims, since the nadir of γ-Cellulose and α-Cellulose locates at the center and the edge, respectively. Therefore, the optimal condition for the steam explosion is 2.74 MPa and 25.3 min, according to the data in **Table 4**. Under the optimal condition, the structure of steam-exploded rice straw showed the characteristics of soft, loose and porous with different sizes distributed though all of the fiber (as shown in **Figure 3a**), which supported further separation of cellulose and lignin. The most of hemicelluloses could be efficiently hydrolyzed,

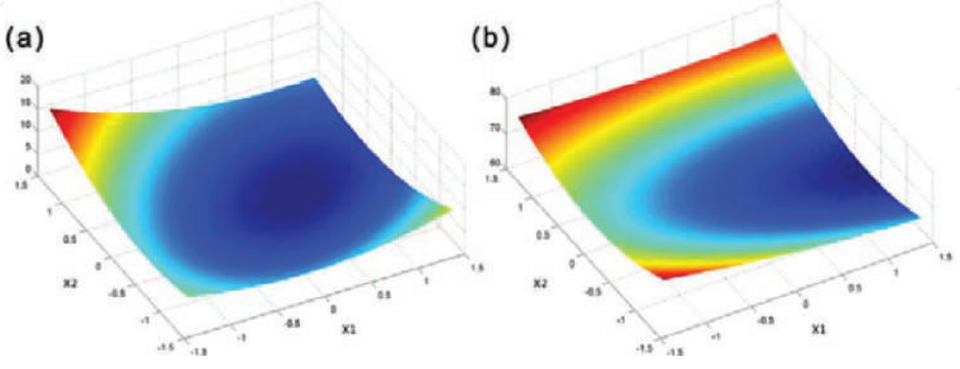

Figure 2. A 3D graphic of dependent factor (referring to final content of γ-cellulose Y_i) vs. independent factors (referring to pressure *X1* and reaction time *X2* of the steam explosion process), (a) according to Eq. (5), and (b) according to Eq. (6).

	γ-Cellulose		α-Cellulose	
	Scaled factor	**Factor**	**Scaled factor**	**Factor**
Pressure *X1* (MPa)	0.481	2.74	1.414	3.20
Reaction time *X2* (min)	0.056	25.3	−0.374	23.1
Content of cellulose Y_i (%)	0.93		62.82	

Table 4. Factor values for the minimum of the content of γ-cellulose and α-cellulose.

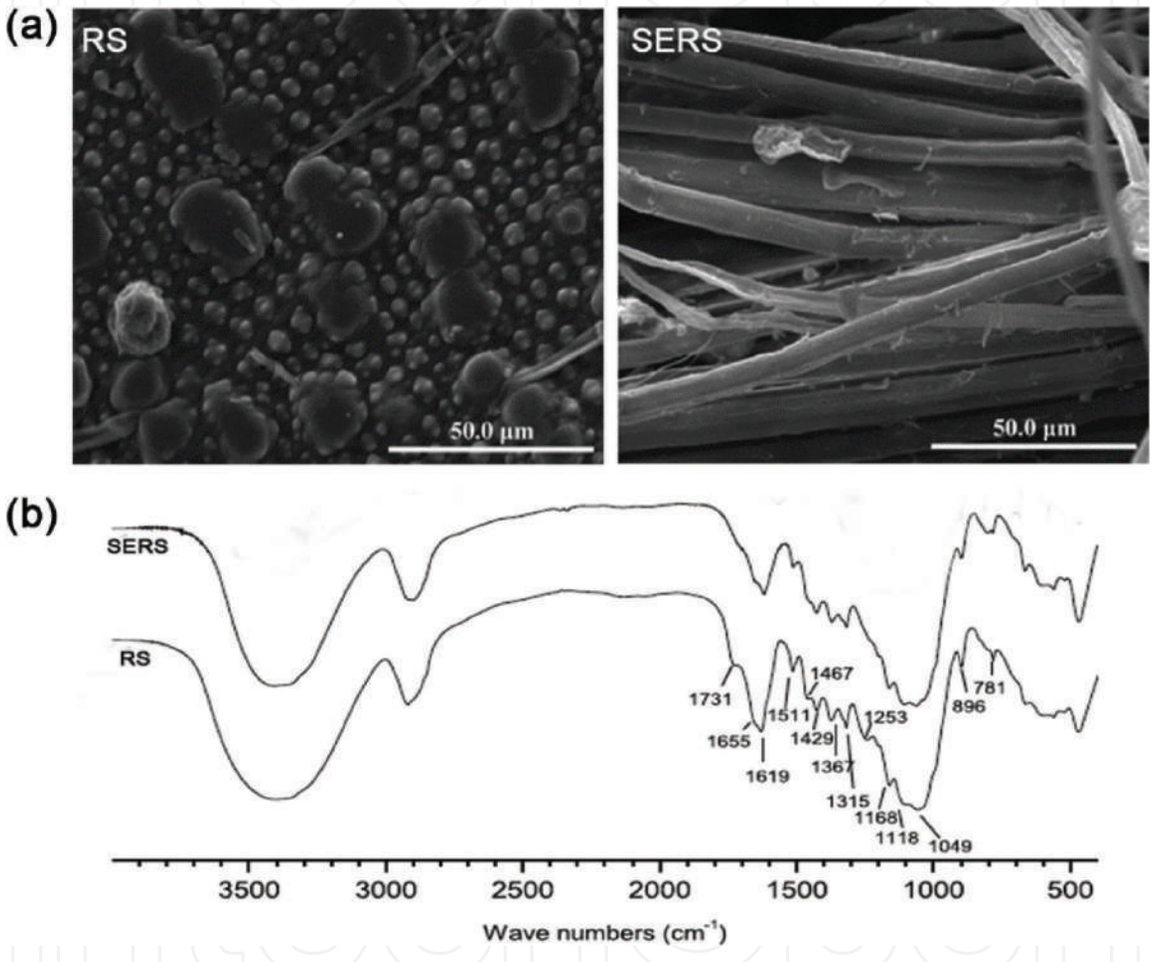

Figure 3. (a) SEM images and (b) FT-IR spectra of rice straw (RS) and steam-exploded rice straw (SERS) [18].

leaving only 1% residual hemicelluloses. However, the majority of cellulose, as well as the fragmentized lignin, were retained in the size, which could be identified by the SEM observations (**Figure 3a**) and the FTIR spectra (**Figure 3b**) [18].

3. Posttreatment of steam-exploded rice straw

3.1. Selective dissolution of cellulose using ionic liquids

Ionic liquids (ILs) are emerging as promising solvents for treatment of lignocelluloses [19–23], due to its low vapor pressures. These solvents are made up of large organic cations and small

inorganic anions, which have the following key properties: (a) they are liquids below 100°C or even at room temperature; (b) high thermal stability; and (c) high polarity [24]. These properties allow to be easily adjusted to dissolve diversity of lignocellulosic biomass [25–27]. Since several kinds of ionic liquids have been found to be non-derivatized solvents for cellulose, they have been applied in such research fields as capturing the portrait of single cellulose molecule [25], and chemical modification of cellulose [19]. In this section, ionic liquids are used in separation of cellulose from steam-exploded rice straw. It is proved to be an efficient and environmentally friendly way to selectively dissolve and then recover cellulose [6].

Four kinds of ionic liquids: 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-allyl-3-methylimidazolium chloride (AMIMCl), 1-benzyl-3-methyl-imidazolium chloride (BnMIMCl) and 1-benzyl-3-methyl-imidazolium trifluoroacetate (BnMIMTFA) have been synthesized according to literature [20]. Their solubility for cellulose and lignin are shown in **Table 5**. The results indicate that BnMIMCl and BnMIMTFA are efficient for dissolving lignin. BMIMCl and AMIMCl are efficient for dissolving cellulose.

AMIMCl is selected as a selective solvent to separate cellulose from the steam-exploded rice straw. The contents of acid-insoluble lignin and celluloses of the steam-exploded rice straw are 14.76 and 64.80% respectively. After dissolving in AMIMCl, there is only 0.90% acid insoluble lignin contained in the recovered cellulose. With a procedure of bleaching by immersing the separated cellulose into hydrogen peroxide aqueous solution together with ozone blowing (about 3.4 g/h produced by SZH5 ozone apparatus, Peking) was needed for bleaching. The bleached cellulose was finally obtained with a yield of 30.73%. The component analysis according to TAPPI standard methods (T 222 om-06 and T 203 cm-09) indicated no detectable acid-insoluble lignin and only 0.85% of hemicelluloses left in the final cellulose. The average degree of polymerization (DP) was 484.

The SEM image and XRD profile of the bleached cellulose are shown in **Figure 4**. As seen in **Figure 4a**, cellulose fibers could be observed clearly with average lengths more than 100 μm. The prominent peak at 22.13° denotes the (002) reflection (as shown in **Figure 4b**). However, the characteristic (101) and (101) peaks (2θ between 15 and 17°) are not as distinct as those in cotton [24], but combine into one broad peak at 15.728°.

The FTIR spectra of the original rice straw, steam-exploded rice straw as well as the bleached cellulose had been provided, **Figure 5a**. The peaks at 1510, 1465 and 1423 cm^{-1} in the sample RS, corresponded to the skeleton stretch of the benzene ring, mainly contributed by lignin. These peaks reduced in steam-exploded sample and disappeared in the bleached cellulose, indicating that the lignin could be removed by selective dissolving of IL. The ^{13}C CP/MAS solid-state NMR spectrum of the bleached cellulose shown in **Figure 5b** suggests that highly purified cellulose is obtained. The chemical shifts at 62 and 64 ppm are assigned to C6 of the primary alcohol group

Ionic liquid	AMIMCl (%)	BMIMCl (%)	BnMIMTFA (%)	BnMIMCl (%)
Cellulose	5.2	4.9	-	-
Lignin	-	-	4.9	3.9

"-" represents nearly no sample can be dissolved.

Table 5. Solubility of the four ILs for cellulose and lignin [6].

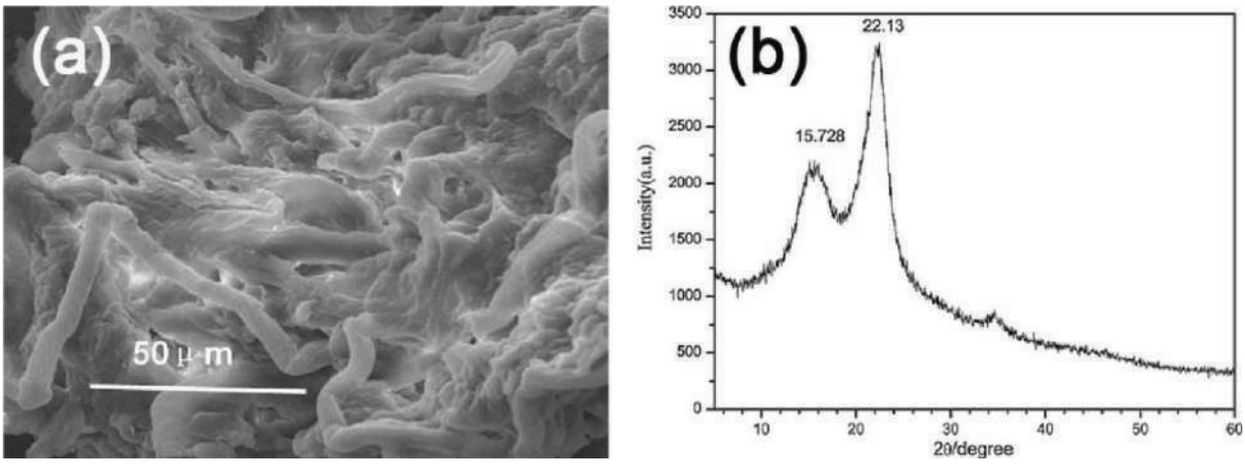

Figure 4. (a) SEM image and (b) XRD profile of bleached cellulose [6].

of cellulose, 71 and 74 ppm attributed to C2, C3 and C5, the ring carbons of cellulose. The peaks at 83 and 88 ppm associated with C4, and 104 ppm associated with C1. The feeble signals at 173 and 20 ppm attributed to the carbonyl and the methyl resonances, respectively.

3.2. Organosolve dissolution of lignin from the steam-exploded straw size

The organosolv process can effectively degrade lignin, which is mainly used osmosis to break and decompose the internal chemical bonds of cellulose and hemicellulose [28–30]. It is considered to be an environmentally friendly way because it can be recycled conveniently, which demonstrates its potential utilization in isolation of lignocellulosic biomass [8]. Moreover, the structure of the dissolved component will be protected from degrading under such moderate conditions, which is benefit for further utilization. The efficient solvent for delignification combined with steam explosion treatment has been realized as the separation of the three components that are cellulose, hemicellulose and lignin. However, few organosolv process

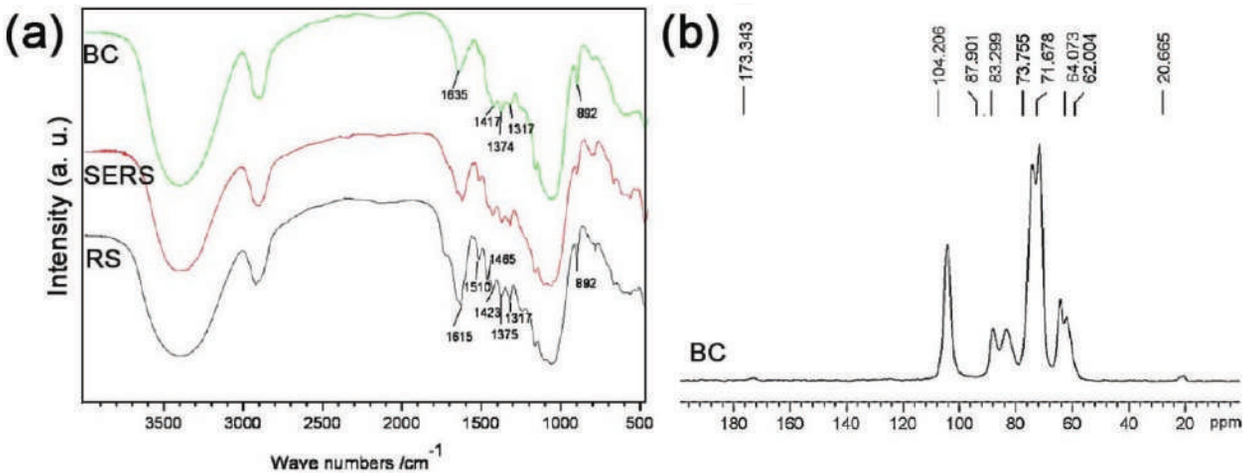

Figure 5. (a)FT-IR spectra and (b) ^{13}C CP/MAS solid-state NMR spectrum of rice straw (RS); steam-exploded rice straw (SERS); bleached cellulose (BC) [6].

http://dx.doi.org/10.5772/intechopen.79014

have been proved attractive as regards efficiency and selectivity, even though intensive researches have been done [31, 32]. In this section, consideration has given on the effect of delignification with mixed solvent from steam-exploded rice straw under ambient pressure [18].

First, the rice straw is pretreated by steam explosion as the optimal conditions mentioned above. The steam-exploded rice straw was then washed with hot water (1:20 g/mL). After that, the residue was delignified by different mixed solvent to obtain crude cellulose. Finally, it was bleached with aqueous solution (1:30 g/mL, pH 11, 55°C) of 2% hydrogen peroxide and 0.2% TAED (tetraacetylethylenediamine) for 5 h.

The mixed solvent system and its results were summarized in **Table 6**. Comparing the delignification efficiency of H_2O-Dimethyl Sulfoxide (DMSO) (sample 7, 63.27%), H_2O-*N*-methylpyrrolidone (NMP) (sample 8, 75.14%) and H_2O-*N*, *N*-dimethylformamide (DMF) (sample 9, 84.78%) solvent systems to H_2O-methanol (sample 1, 57.13%), one could conclude that water-aprotic solvent system was better than water-protic solvent system for delignification. The delignification efficiency of H_2O-methanol could be further improved to 79.99% with aniline additive as the catalyst (sample 6). Similarly, aniline additive as a catalyst in the H_2O-DMF solvent system resulting in the efficiency improvement of delignification from 84.78 (sample 9) to 95.04% (sample 10).

Conclusively, the H_2O-DMF-aniline solvent system (in a volume ratio of 20:10:1) demonstrated to be the most efficient solvent for removing lignin from the steam-exploded rice straw because the DMF and aniline included amino groups might improve the dissolution of lignin.

The FTIR spectrum of the original rice straw, the steam-exploded rice straw, the delignified sample with H_2O-DMF-aniline and bleached cellulose shown **Figure 6a** indicated that the

No.	Solvent system[a]	Additives	Lignin residue (wt%)	Delignification[b] (%)
1	H_2O-methanol	—	7.52	57.13
2	H_2O-methanol	Formic acid	5.09	70.98
3	H_2O-methanol	Terephthalic acid	5.10	73.93
4	H_2O-methanol	Salicylic acid	2.89	77.33
5	H_2O-methanol	Sodium hydroxide	3.92	69.25
6	H_2O-methanol	Aniline	3.51	79.99
7	H_2O-DMSO	—	6.45	63.27
8	H_2O-NMP	—	4.36	75.14
9	H_2O-DMF	—	2.67	84.78
10	H_2O-DMF	Aniline	0.87	95.04

[a]Represents the residual cellulose-enriched fractions obtained with water, organic solvent and additives in ratios of 20:10:1 (v: v: v).

[b]The acid-insoluble lignin content in the steam-exploded rice straw is measured to be 12.75%.

Table 6. Influence of the composition of mixed solvent on the delignification process [18].

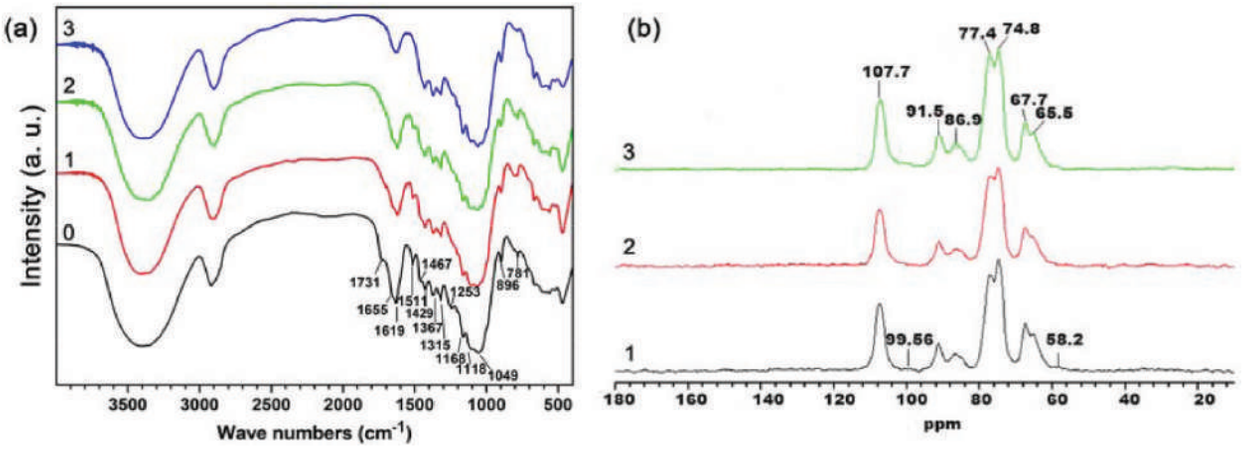

Figure 6. (a) FTIR spectra and (b) ^{13}C-NMR spectra of different samples (0, original rice straw); steam-exploded rice straw (1, SERS); H_2O-DMF-aniline delignified rice straw (2, DERS); bleached cellulose (3, BC) [18].

lignin in straw could be removed and obtained pure cellulose because the absorptions at 1511 and 1429 cm^{-1} assigned to the aromatic C=C stretch from aromatic ring in lignin became weak after the steam explosion (spectrum SERS) and delignification (spectrum DERS), and finally disappeared in the bleached cellulose (spectrum BC) [18].

Figure 6b indicated the ^{13}C CP/MAS solid-state NMR spectra of the steam-exploded rice straw (SERS), delignified rice straw (DERS) and bleached cellulose (BC).All of these spectra were dominated by the resonances attributable to cellulose. Notably, two small peaks at 99.5 and 58.2 ppm in the spectrum of steam-exploded rice straw (pattern SERS) were assigned to lignin and they nearly disappear in spectrum DERS, BC, which were the delignified cellulose with the water-DMF-aniline solvent system and bleached cellulose, respectively.

3.3. Biological removal of lignin from the steam-exploded straw size

Biological treatments employ microorganisms and their enzyme systems to break down the lignin present in lignocellulosic biomass. This approach has recently attracted increased attention because of its mild condition, low energy consumption, and the absence of pollution [33, 34]. Among the microorganisms those are capable of degrading lignocelluloses, white rot fungi has a higher selectivity toward lignin with lower energy input, as well as being environmentally friendly [35].

One white rot fungus, *Phanerochaete chrysosporium* (*P. chrysosporium*), harbors at least 10 lignin peroxidases (LiP), five manganese peroxidases (MnP), and several copper oxidases in its lignin-degrading system [36, 37]. Combinatorial treatment of steam explosion and biological treatment has been considered as an effective method of separating components for various kinds of biomass. Chen et al. [38] reported the effects of the solid-state fermentation (SSF) conditions on biodegradation of steam-exploded wheat straw with *P. chrysosporium*. Under the optimum conditions of SSF, the degradation amount of lignin reached 60% on the 5th day. Zhang et al. [39] indicated that steam explosion is an important pretreatment method for biodegradation of lignin in rice straw. After steaming under 2.5 MPa for 25 min, then completely decompressed within 3 min, the steam-exploded straw was collected and dried for biodegradation treatment. In their study, the degradation rate of lignin was 31.23% without steam explosion, and 55.40%

lignin loss rate had been found on day 30 after steam explosion pretreatment. A two-stage process proposed by Zhou et al. [40] was based on the pretreatment of steam explosion and followed by a *P. chrysosporium* post-treatment for the isolation of cellulose.

As the above processes, the orthogonal experiments (using L_{16} $(4)^5$ orthogonal table) were designed (**Table 8**) to investigate the relationship between the delignification in SERS and the five factors. Each factor had been set based on the pretest results and a literature review (**Table 7**). Curves of the factors vs. the delignification was shown in **Figure 7**.

According to **Table 8**, the maximum lignin loss rate, 64.25%, was obtained with the conditions of 1% spore suspension, 70% moisture content, 0.1% T-80, initial pH of 5.0, and 28 days of fermentation. The experimental outcomes could not be used as the best SSF conditions, so the orthogonal analysis should be performed. **Table 8** shows the results of orthogonal analysis for five factors used in the fermentation process and the order of importance of these factors on lignin removal was E > C > B > D > A. Based on the *k* value of the testing factors, the optimum process for fermentation is $A_3B_3C_2D_3E_4$, corresponding to 1.5% spore suspension, 0.3% T-80, 70% moisture, initial pH of 5.0, and 28 days of SSF.

According to the analysis presented above, the most important factor for delignification was SSF time. However, there was no top value of SSF time vs. delignification unlike the other four factors as shown in **Figure 7**. Hence, the effect of SSF time required further study.

Moisture was found to be significant to the delignification by *P. chrysosporium*. Water in SSF systems shows functions of transporting the nutrients and metabolites, which can contribute to the stability of the cellular and molecular structures. As displayed in **Figure 7**, until the moisture levels (70 and 75%), the delignification increased with increase of moisture. However, the delignification decreased after moisture exceeded 75% because the high moisture hampered the diffusion of oxygen into the liquid and solid phases thus limited aerobic SSF.

Figure 8 shows the effect of SSF time on the removal of lignin. The experimental results satisfactorily fitted the Boltzmann model with the decisive coefficient R^2 = 0.9983. The lignin content of the steam-exploded rice straw was efficiently degraded after a prolonged period. Nearly half of the highest lignin removal rate was obtained on the 7th day of fermentation. When the treatment time of using *P. chrysosporium* was 10 days, the lignin removal increased to 50.13%. Thereafter, the lignin removal rate decreased and tends to stabilize after 12 days.

Although the lignin degradation of steam-exploded rice straw is very important, too much weight loss is unexpected. The relationship between the SSF time and weight loss is shown

No.	Factor	Level 1	Level 2	Level 3	Level 4
A	Spore suspensions concentration (%)	0.5	1.0	1.5	2.0
B	T-80 concentration (%)	0.1	0.2	0.3	0.4
C	Moisture content (%)	65	70	75	80
D	Initial pH	3	4	5	6
E	SSF time (day (d))	7	14	21	28

Table 7. Factors levels for the orthogonal experiments [40].

Test no.	Factors					Delignification (%)
	A	B	C	D	E	
1	0.5	0.1	65	3	7	16.63
2	0.5	0.2	70	4	14	49.68
3	0.5	0.3	75	5	21	56.37
4	0.5	0.4	80	6	28	37.92
5	1.0	0.1	70	5	28	64.25
6	1.0	0.2	65	6	21	52.78
7	1.0	0.3	80	3	14	28.75
8	1.0	0.4	75	4	7	17.02
9	1.5	0.1	75	6	14	48.43
10	1.5	0.2	80	5	7	8.65
11	1.5	0.3	65	4	28	62.65
12	1.5	0.4	70	3	21	53.46
13	2.0	0.1	80	4	21	39.15
14	2.0	0.2	75	3	28	57.97
15	2.0	0.3	70	6	7	24.06
16	2.0	0.4	65	5	14	43.06
K_1	160.60	168.46	175.81	156.81	66.36	
K_2	162.80	169.08	191.45	168.50	170.61	
K_3	173.19	171.83	179.79	173.02	201.76	
K_4	164.93	152.15	114.47	163.19	222.79	
k_1 [a]	40.15	42.12	43.95	39.20	16.59	
k_2 [a]	40.70	42.27	47.86	42.12	42.65	
k_3 [a]	43.30	42.96	44.95	43.25	50.44	
k_4 [a]	41.23	38.04	28.62	40.80	55.70	
R [b]	3.15	4.92	19.24	4.05	39.11	

[a] k_1, k_2, k_3, and k_4 are the mean values of the sum of the evaluation indexes of all levels. By comparing k values, the optimal levels of the factors can be confirmed.

[b] The range of factors (R = Max(k_j)− Min(k_j)) indicates the function of the corresponding factor. The larger value of R means the greater impact of the level of the factor on the experimental index.

Table 8. Experimental setup together with results of *P. chrysosporium* delignification [40].

in **Figure 9**, which turned out to be a linear relationship with decisive coefficient $R^2 = 0.99843$. The weight loss of SERS is proportional to the SSF time, differing from the results shown in **Figure 8**. Weight loss of SERS might be attributed to the removal of lignin and hemicellulose over 10 days of fermentation, after which the degradation of cellulose gradually became a major factor of SSF.

http://dx.doi.org/10.5772/intechopen.79014

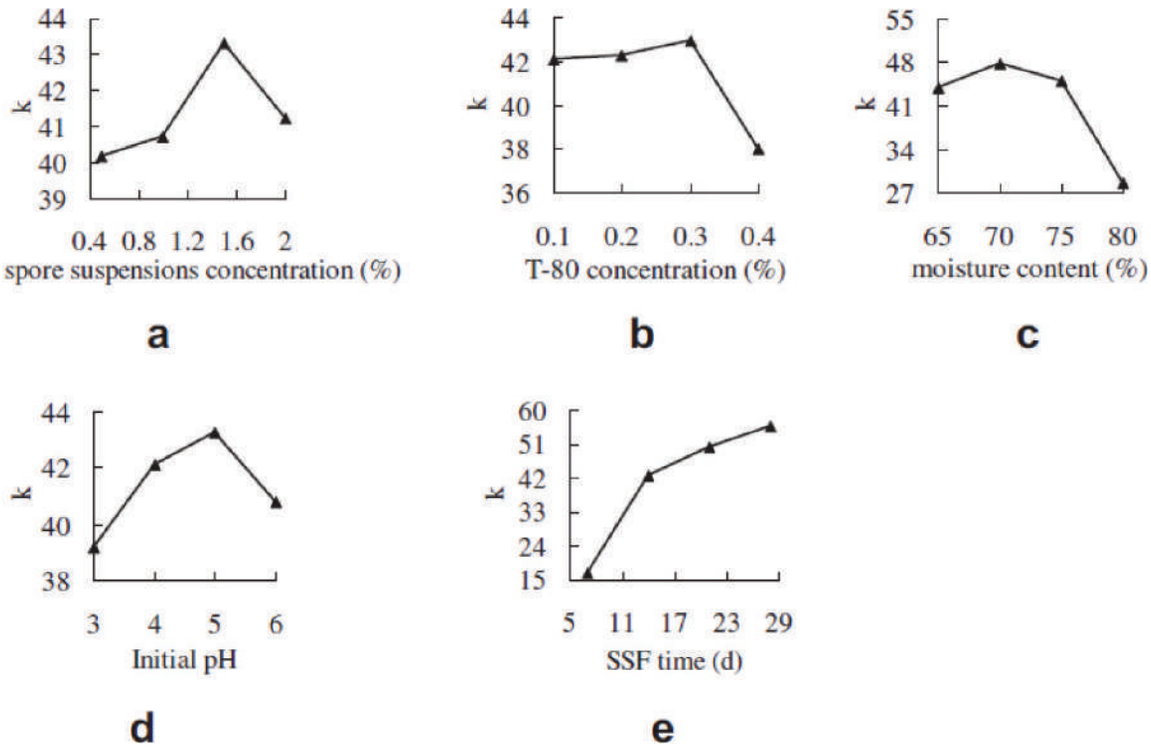

Figure 7. Curves of the factors vs. delignification [40].

In comparison with the FTIR spectrum of untreated SERS (**Figure 10a**), prominent changes could be obtained in the samples degraded after different SSF timings. The increase in the intensity of peak at 1650 cm^{-1} showed higher abundance of C=O groups of lignin, demonstrating the aromatic lignin moieties altered by oxidation with lignin biodegradation. In addition, peaks at 1510 and 1431 cm^{-1} turned weakening with increasing treatment time, implying the

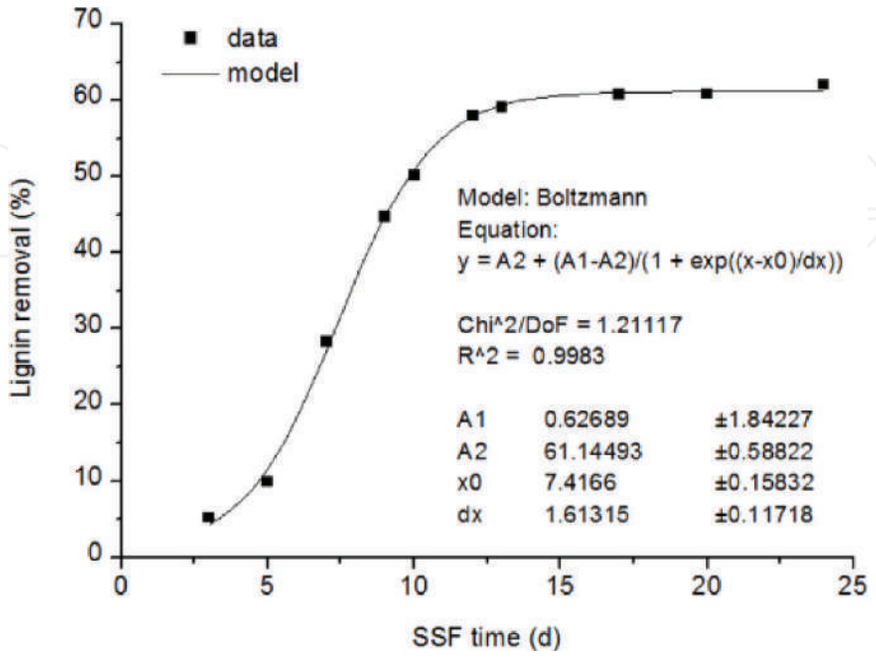

Figure 8. The effect of SSF time on the removal of lignin [40].

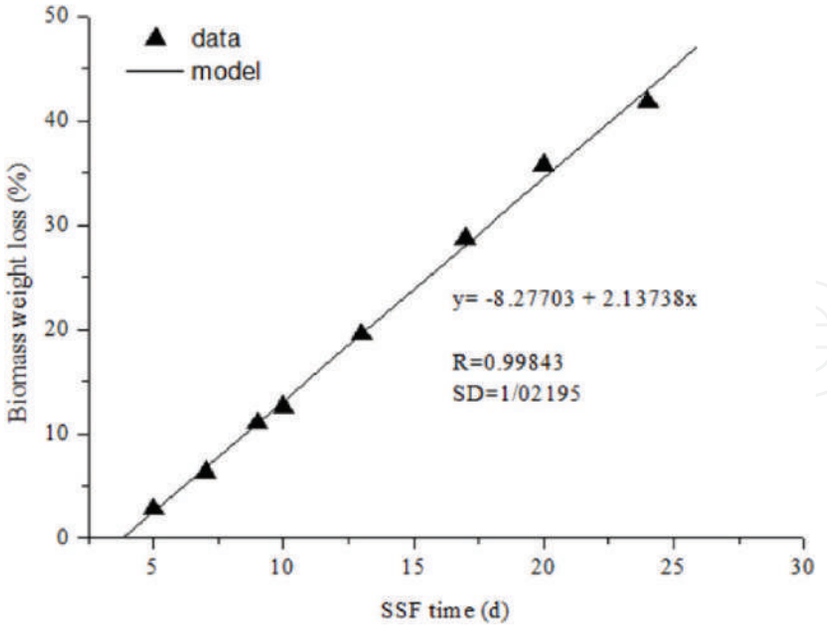

Figure 9. The effect of SSF time on the weight loss of SERS [40].

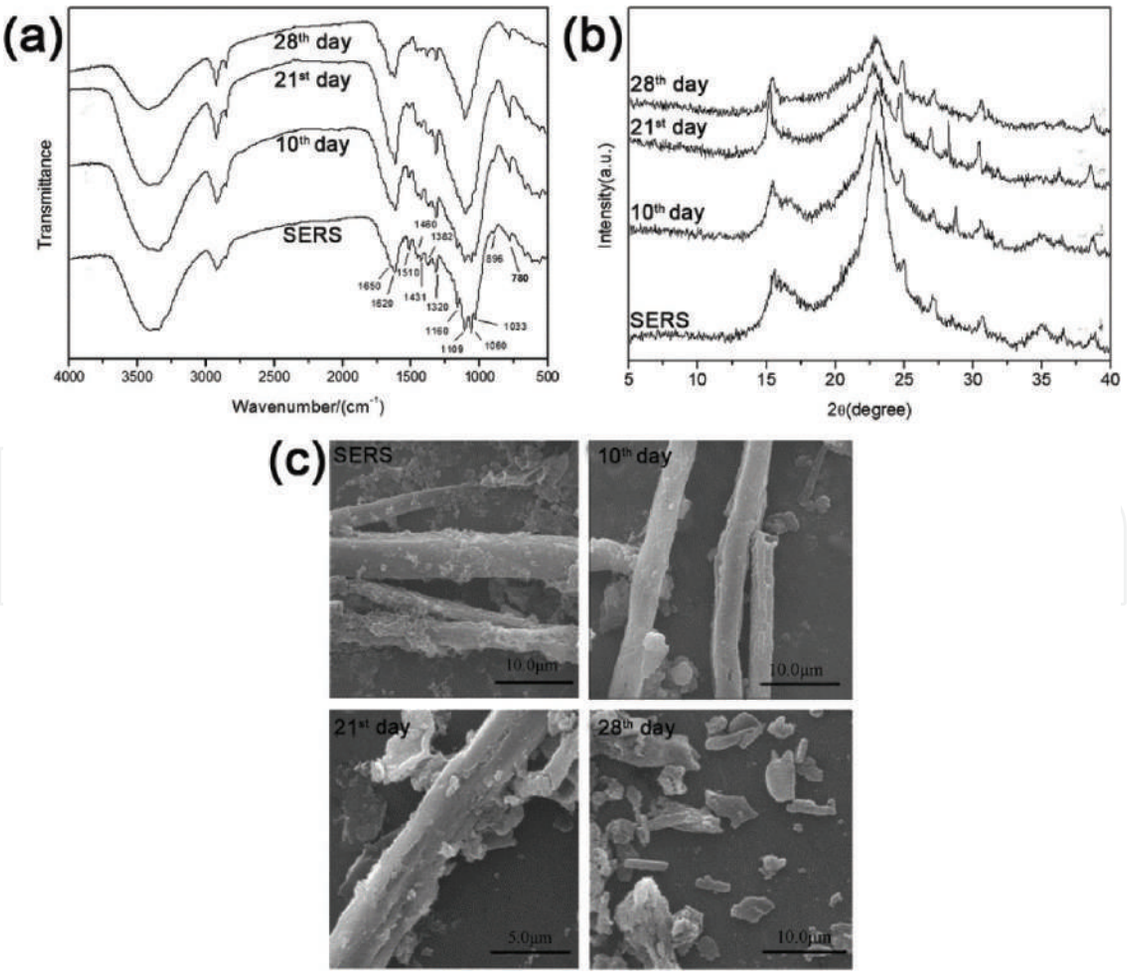

Figure 10. (a) FTIR spectra, (b) XRD patterns, and (c) morphologies of SERS before and after SSF with *P. chrysosporium*.

aromatic skeletal carbon of lignin was destroyed by *P. chrysosporium*. The peaks at 896, 1060, and 1160 cm^{-1} disappeared with increasing SSF time, showing that the structure of cellulose has been degraded after longer treatment time. Peaks observed near 23.11° (**Figure 10b**) represent diffractions of the (002) crystal plane, indicating that the crystal type of cellulose in SERS is cellulose type-I in nature (as shown in **Figure 10b**). Fermentation appeared not to change the crystal type of cellulose. With increasing SSF time, the peak height of the (002) crystal plane decreased and the peak width at half height increased compared with untreated SERS. The morphologies of the samples before and after bio treatment had been examined by SEM (**Figure 10c**) to visually demonstrate the process of delignification and cellulose degradation by *P. chrysosporium*.

4. High-value applications of cellulose isolated from straw

All-cellulose composites (AACs) have been proposed to meet the interfacial problem in the cellulose-based composites, where both the reinforcement phase and matrix are cellulose [41–43]. Zhou et al. [44] reported that ACCs, with microcrystalline cellulose (MCC) as the matrix and the straw cellulose fibers (SCFs) as the reinforcement agent exhibited an ultra-high tensile strength (650.2 MPa, **Figure 11**).

The mechanism for the high performance of alkali-treated SCF (N-SCF) and activated SCF (A-SCF) reinforced ACCs are shown in **Figure 12**. For the ACCs/N-SCF sample (**Figure 12a**), the reinforcement mechanism is possibly related to the removal of impurities and the increase of aspect ratio. For the ACCs/A-SCF sample (**Figure 12b**), the reinforcement mechanism can be possibly attributed to the fact that both A-SCF and MCC experience the same activation process. Due to successively pre-swell with solvents (water, ethanol, *N*, *N*-dimethylacetamide) gradually reducing polarity, the

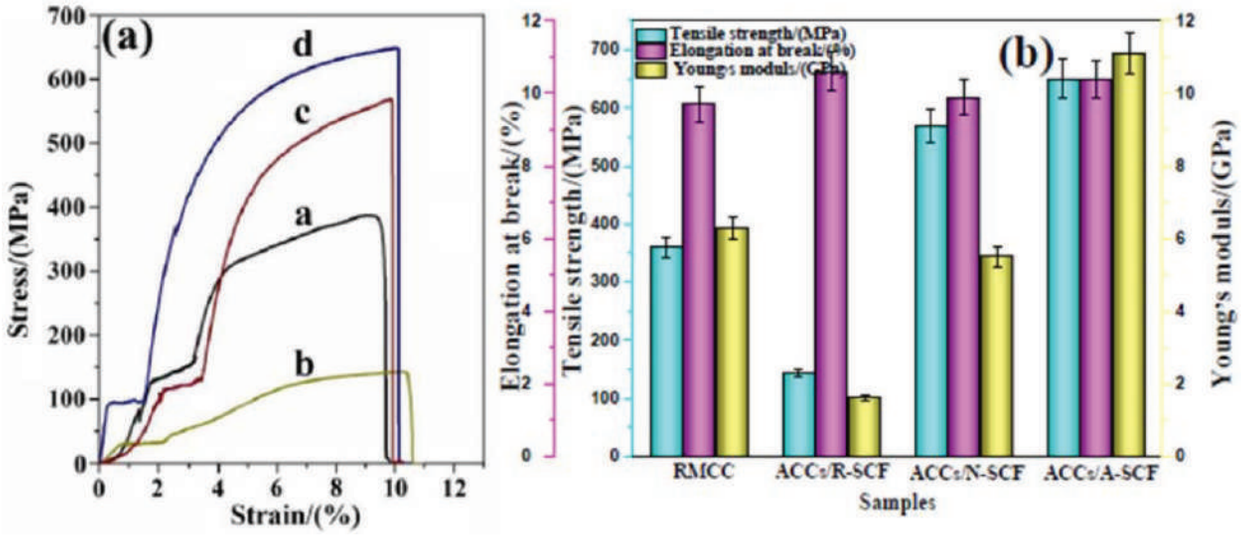

Figure 11. (a) Typical engineering stress–strain curves of the samples, (b) the corresponding tensile properties, where, a: Regenerated MCC, b: ACCs/activated SCF (A-SCF), c: ACCs/alkali-treated (N-SCF), and d: ACCs/activated SCF [44].

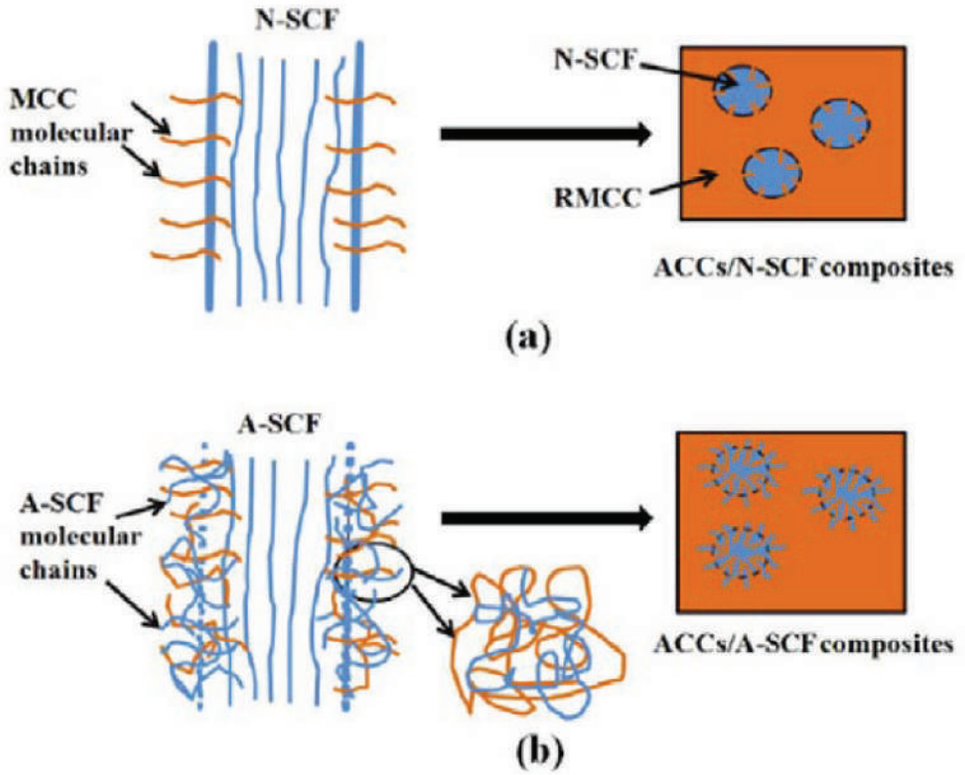

Figure 12. Schematic representations showing the reinforcement mechanism of the N-SCF (a) and the A-SCF (b) in the ACCs [44].

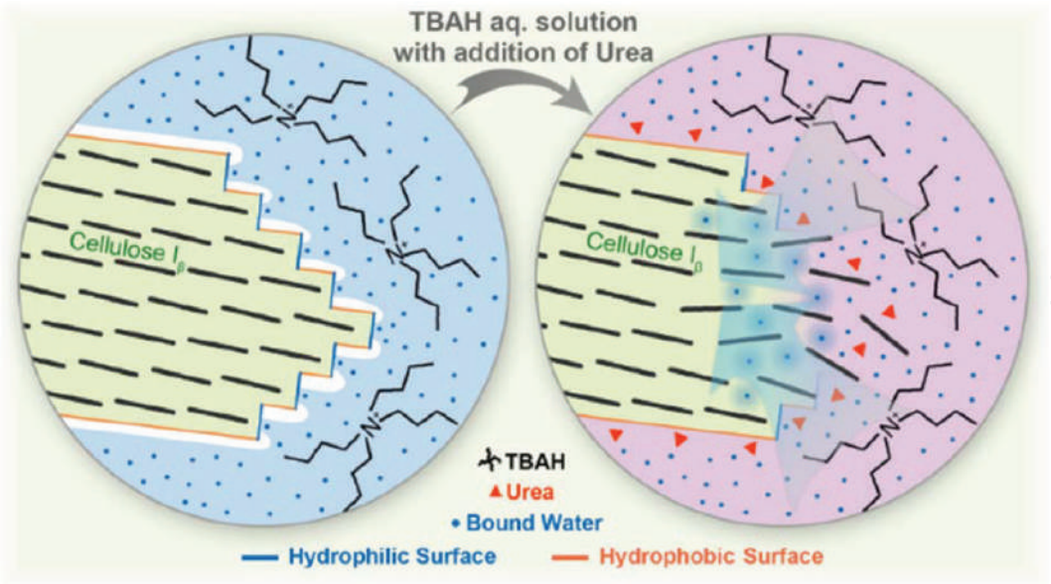

Figure 13. Schematic illustration for the mechanism of TBAH/urea aqueous solution dissolving cellulose. These two diagrams display various interfacial resistances between the crystal surface of natural cellulose and the solvent [49].

A-SCF and MCC molecular chains in SCF and MCC could be partially dissolved and penetrated into each other, resulting in improving entanglement density of molecular chains on the fiber surface.

Besides, the isolated cellulosic fibers of about 2–16 wt% can be introduced into the cement with a slurry vacuum de-watering technique [45]. It was found that the flexural strength and fracture toughness of the optimal sample were increased by 24.3% and 45 times, respectively.

Effective solvent system for cellulose dissolution is a long-standing goal due to the abundant hydroxyl groups on the cellulose chain form a strong, three-dimensional intermolecular and intramolecular hydrogen bonding network [46, 47]. Therefore, Zhou et al. [48] developed a new aqueous solvent for cellulose based on the quaternary ammonium hydroxide (TBAH). It was found that cellulose can be efficiently dissolved in a 40 wt% TBAH aq. solution under a cooling condition. The mechanism for the dissolution is believed to be the match of amphiphilicity between the solvent and cellulose crystal. Then, Zhou et al. [49] studied the effects of urea to the dissolution of cellulose in TBAH. It was found that a hybrid hydrate of TBAH and urea formed. Urea can serve as a hydrophobic contributor, by which the amphiphilic property of the solvent system can be adjusted. With a suitable amphiphilicity, interfacial resistance between the solvent and crystal surface can be reduced so that the crystal of natural cellulose can be effectively infiltrated and subsequently dissolved by the solvent. The schematic dissolution process of the cellulose is shown in **Figure 13**.

5. Conclusions

The steam explosion process is realized as a promising pre-treatment for the separation of cellulose from natural biomasses. It can make most of the hemicellulose hydrolyze and part of the lignin degrade, which results in loose and porous structures, which could ultimately support further separation of cellulose and lignin. One kind of ionic liquids, 1-allyl-3-methylimidazolium chloride (AMIMCl), is selected for the extraction of cellulose, due to its especially selective solubility for cellulose rather than lignin. This process with ionic liquids shows advantages of efficiency, environmentally friendly, and recyclability character. Isolation of cellulose with the organic solvent system that composes of H_2O-DMF-aniline has proved that it also been considered as an environmental-friendly approach, and up to 95.04% lignin can be dissolved out from the steam-exploded rice straw, leaving quite a small amount of hemicellulose (<1%) and lignin (<0.85%). There is no obvious decrease in the degree of cellulose crystallinity during the delignification and bleaching processes. Approximately 58% lignin can be removed under selective delignification of the steam-exploded rice straw by *P. chrysosporium*. The isolated cellulose fiber from the rice straw can serve as a reinforcement material for the advanced mechanical property of composites. The prepared ACCs exhibit an ultrahigh tensile strength. The cellulose/cement composites show a remarkable improvement in the flexural strength and fracture toughness. Cellulose can be efficiently dissolved in a 40 wt% TBAH aq. solution under a cooling process.

Acknowledgements

The authors acknowledge the financial support of the National Natural Science Foundation of China (No. 51303151), the National Key Technology R&D Program of the Ministry of Science and Technology of China (No. 2011BAE11B01), the Science and Technology Planning Project of Sichuan Province (No. 2016GZ0224,2016CZYZF0003), Sichuan Province Youth Science and Technology Innovation Team (No. 2016TD0026), Sichuan Province Science and Technology Innovation Talent Project (No. 2017072), and the Fundamental Research Funds for the Central Universities (No. 2682016CX069).

Author details

Guangjun Gou[1], Wei Wei[1], Man Jiang[1], Shengli Zhang[2], Tingju Lu[1], Xiaoli Xie[3], Fanbin Meng[1] and Zuowan Zhou[1]*

*Address all correspondence to: zwzhou@swjtu.edu.cn and jiangman1021@swjtu.edu.cn

1 Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu, Sichuan, China

2 Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu, Sichuan, China

3 State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang, China

References

[1] Huang CF, Jiang YF, Guo GL, Whang WS. Method of 2, 3-butanediol production from glycerol and acid-pretreated rice straw hydrolysate by newly isolated strains: Pre-evaluation as an integrated biorefinery process. Bioresource Technology. 2013;**135**:446-453

[2] Singh R, Shukla A, Tiwari S, Srivastava M. A review on delignification of lignocellulosic biomass for enhancement of ethanol production potential. Renewable and Sustainable Energy Reviews. 2014;**32**:713-728

[3] Cheali P, Posada JA, Gernaey KV, Sin G. Grading of lignocellulosic biorefinery to value added chemicals: Sustainability and economics of bioethanol-derivatives. Biomass and Bioenergy. 2015;**75**:282-300

[4] Santos F, Machado G, Faria D, Lima J, Marçal N, Dutra E, Souza G. Productive potential and quality of rice husk and straw for biorefineries. Biomass Conversion and Biorefinery. 2017;**7**(1):117-126

[5] Sun JX, Xu F, Geng ZC, Sun RC. Comparative study of cellulose isolated by totally chlorine-free method from wood and cereal straw. Journal of Applied Polymer Science. 2005;**97**:322-335

[6] Jiang M, Zhao MM, Zhou ZW, Huang T, Chen XL, Wang Y. Isolation of cellulose with ionic liquid from steam exploded rice straw. Industrial Crops and Products. 2011;**33**(3):734-738

[7] Cheng J, Huang R, Li T, Zhou J, Cen K. Physicochemical characterization of wet microalgal cells disrupted with instant catapult steam explosion for lipid extraction. Bioresource Technology. 2015;**191**:66-72

[8] Ostovareh S, Karimi K, Zamani A. Efficient conversion of sweet sorghumstalks to biogas and ethanol using organosolv pretreatment. Industrial Crops and Products. 2015;**66**:170-177

[9] Rouches E, Herpoël-Gimbert I, Steyer J, Carrere H. Improvement of anaerobic degradation by white-rot fungi pretreatment of lignocellulosic biomass: A review. Renewable and Sustainable Energy Reviews. 2016;**59**:179-198

[10] Elgharbawy AA, Alam MZ, Moniruzzaman M, Goto M. Ionic liquid pretreatment as emerging approaches for enhanced enzymatic hydrolysis of lignocellulosic biomass. Biochemical Engineering Journal. 2016;**109**:252-267

[11] Vochozka M, Maroušková A, Váchal J, Straková J. Economic and environmental aspects of steam-explosion pretreatment. Waste and Biomass Valorization. 2016;**7**(6):1549-1554

[12] Brownell HH, Yu EKC, Saddler JN. Steam-explosion pretreatment of wood: Effect of chip size, acid, moisture content and pressure drop. Biotechnology and Bioengineering. 1986;**28**:792-801

[13] Monavari S, Gable M, Zacchi G. Impact of impregnation time and chip size on sugar yield in pretreatment of soft wood for ethanol production. Bioresource Technology. 2009;**100**:6312-6316

[14] Chen HY, Liu JB, Chang X, Chen DM, Xue Y, Liu P, Lin HL, Han S. A review on the pretreatment of lignocellulose for high-value chemicals. Fuel Processing Technology. 2017;**160**:196-206

[15] Heikkinen H, Elder T, Maaheimo H, Rovio S, Rahikainen J, Kruus K, Tamminen T. Impact of steam explosion on the wheat straw lignin structure studied by solution-state nuclear magnetic resonance and density functional methods. Journal of Agricultural and Food Chemistry. 2014;**62**:10437-10444

[16] Jacquet N, Maniet G, Vanderghem C, Delvigne F, Richel A. Application of steam explosion as pretreatment on lignocellulosic material: A review. Industrial Crops and Products. 2015;**54**(10):2593-2598

[17] López-Linares JC, Ballesteros I, Tourán J, Cara C, Castro E, Ballesteros M, Romero I. Optimization of uncatalyzed steam explosion pretreatment of rapeseed straw for biofuel production. Bioresource Technology. 2015;**190**:97-105

[18] Mu CY, Jiang M, Zhu J, Zhao MM, Zhu SH, Zhou ZW. Isolation of cellulose from steam-exploded rice straw with aniline catalyzing dimethyl formamide aqueous solution. Renewable Energy. 2014;**63**:324-329

[19] Fu D, Mazza G. Optimization of processing conditions for the pretreatment of wheat straw using aqueous ionic liquid. Bioresource Technology. 2011;**102**:8003-8010

[20] Fu D, Mazza G. Aqueous ionic liquid pretreatment of straw. Bioresource Technology. 2011;**102**:7008-7011

[21] deCosta Lopes AM, Joan KG, Rubik DF, Bogel-Lukasik E, Duarte LC, Andreaus J, Bogel-Lukasik R. Pre-treatment of lignocellulosic biomass using ionic liquids: Wheat straw fractionation. Bioresource Technology. 2013;**142**:198-208

[22] daCarneiro AP, Rodriguez O, Macedo EA. Dissolution and fractionation of nut shells in ionic liquids. Bioresource Technology. 2017;**227**:188-196

[23] Lozano P, Bernal B, Recio I, Belleville MP. A cyclic process for full enzymatic saccharification of pretreated cellulose with full recovery and reuse of the ionic liquid 1-butyl-3-methylimidazolium chloride. Green Chemistry. 2012;**14**:2631-2637

[24] Zavrel M, Bross D, Funke M, Büchs J, Spiess AC. High-throughput screening for ionic liquids dissolving (ligno-) cellulose. Bioresource Technology. 2009;**100**:2580-2587

[25] Wan ZZ, Li L, Cui SX. Capturing the portrait of isolated individual natural cellulose molecules. Biopolymers. 2008;**89**(12):1170-1173

[26] Dyson PJ, Grossel MC, Srinivasan N, Vine T, Welton T, Williams DJ, White AJP, Zigras T. Organometallic synthesis in ambient temperature chloroaluminate(III) ionic liquids. Ligand exchange reactions of ferrocene. Journal of the Chemical Society, Dalton Transactions. 1997:3465-3469

[27] Reddy N, Yang YQ. Preparation and characterization of long natural cellulose fibers from wheat straw. Journal of Agricultural and Food Chemistry. 2007;**55**(21):8570-8575

[28] Mupondwa E, Li X, Tabil L, Sokhansanj S, Adapa P. Status of Canada's lignocellulosic ethanol: Part I: Pretreatment technologies. Renewable and Sustainable Energy Reviews. 2017;**72**:178-190

[29] Zhao X, Cheng K, Liu D. Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. Applied Microbiology and Biotechnology. 2009;**82**:815-827

[30] Papatheofanous M, Billa E, Koullas D, Monties B, Koukios E. Two-stage acid-catalyzed fractionation of lignocellulosic biomass in aqueous ethanol systems at low temperatures. Bioresource Technology. 1995;**54**:305-310

[31] Ziaie-Shirkolaee Y, Mohammadi-Rovshandeh J, Rezayati-Charani P, Khajeheian MB. Influence of dimethyl formamide pulping of wheat straw on cellulose egradation and comparison with Kraft process. Bioresource Technology. 2008;**99**:3568-3578

[32] Rodríguez A, Serrano L, Moral A, Pérez A, Jiménez L. Use of high-boiling point's organic solvents for pulping oil palm empty fruit bunches. Bioresource Technology. 2008;**99**:1743-1749

[33] Mishra V, Jana AK, Jana MM, Gupta A. Enhancement in multiple lignolytic enzymes production for optimized lignin degradation and selectivity in fungal pretreatment of sweet sorghum bagasse. Bioresource Technology. 2017;**236**:49-59

[34] Mosier N, Wyman C, Dale B, Elander R, Lee Y, Holtzapple M, Ladisch M. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresource Technology. 2005;**96**:673-686

[35] Martín-Sampedro R, Fillat Ú, Ibarra D, Eugenio ME. Use of new endophytic fungi as pretreatment to enhance enzymatic saccharification of *Eucalyptus globulus*. Bioresource Technology. 2015;**196**:383-390

[36] Janse BJH, Gaskell J, Akhtar M, Cullen D. Expression of *Phanerochaete chrysosporium* genes encoding lignin peroxidases, manganese peroxidases, and glyoxal oxidase in wood. Applied and Environmental Microbiology. 1998;**64**:3536-3538

[37] Martinez D, Larrondo LF, Putnam N, Gelpke MD, Huang K, Chapman J, Helfenbein KG, Ramaiya P, Detter JC, Larimer F, Coutinho PM, Henrissat B, Berka R, Cullen D, Rokhsar D. Genome sequence of the lignocellulose degrading fungus *Phanerochaete chrysosporium* strain RP 78. Nature Biotechnology. 2004;**22**:695-700

[38] Cheng HZ, Xu FJ, Li ZH. Solid-state production of biopulp by *Phanerochaete chrysosporium* using steam-exploded wheat straw as substrate. Bioresource Technology. 2002;**81**:261-263

[39] Zhang LH, Li D, Wng LJ, Zhang L. Effect of steam explosion on biodegradation of lignin in wheat straw. Bioresource Technology. 2008;**99**:8512-8515

[40] Zhang SL, Jiang M, Zhou ZW, Zhao MM, Li Y. Selective removal of lignin in steam-exploded rice straw by *Phanerochaete chrysosporium*. International Biodeterioration and Biodegradation. 2012;**75**:89-95

[41] Kalka S, Huber T, Steinberg J, Baronian K, Müssig J, Staiger MP. Biodegradability of all-cellulose composite laminates. Composites Part A: Applied Science and Manufacturing. 2014;**59**:37-44

[42] Huber T, Pang S, Staiger MP. All-cellulose composite laminates. Composites Part A: Applied Science and Manufacturing. 2012;**43**:1738-1745

[43] Piltonen P, Hildebrandt NC, Westerlind B, Valkama JP, Tervahartiala T, Illikainen M. Green and efficient method for preparing all-cellulose composites with NaOH/urea solvent. Composites Science and Technology. 2016;**135**:153-158

[44] Wei X, Wei W, Cui YH, Lu TJ, Jiang M, Zhou ZW, Wang Y. All-cellulose composites with ultra-high mechanical properties prepared through using straw cellulose fiber. RSC Advances. 2016;**6**:93428-93435

[45] Xie XL, Zhou ZW, Jiang M, Xu XL, Hui D. Cellulosic fibers from rice straw and bamboo used as reinforcement of cement-based composites for remarkably improving mechanical properties. Composites Part B Engineering. 2015;**78**:153-161

[46] Nishiyama Y, Langan P, Chanzy H. Crystal structure and hydrogen-bonding system in cellulose 1 beta from synchrotron X-ray and neutron fiber diffraction. Journal of the American Chemical Society. 2002;**124**:9074-9082

[47] Abe M, Fukaya Y, Ohno H. Fast and facile dissolution of cellulose with tetrabutylphosphonium hydroxide containing 40 wt% water. Chemical Communications. 2012;**48**:1808-1810

[48] Wei W, Wei X, Gou GJ, Jiang M, Xu XL, Wang Y, Hui D, Zhou ZW. Improved dissolution of cellulose in quaternary ammonium hydroxide by adjusting temperature. RSC Advances. 2015;**5**:39080-39083

[49] Wei W, Meng FB, Cui YH, Jiang M, Zhou ZW. Room temperature dissolution of cellulose in tetrabutylammonium hydroxide aqueous solvent through adjustment of solvent amphiphilicity. Cellulose. 2017;**24**:49-59