

Engineering Cellulose Fibers for High-Value Added Products for Pulp & Paper Industry

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ABSTRACT

Cellulose fibers is one of the most abundant in nature. It has many distinctive features: abundant in nature, biodegradable, non-toxic, eco-friendly, sustainable, easy to fabricate, hydrophilic, and cost-effective.

Cellulose fibers, known as pulp, is produced from cellulose-containing materials by the pulping process. As the raw material, wood has been most commonly used while recycled pulp has been also used to some degree. Thus, pulp usually refers to wood pulp. Generally, the pulp and paper industry is regarded as the commodity market where the cost should be much more important than the quality. It also belongs to a mature market where the growth is slow, or even in decline. Accordingly, technological development has been rather stagnant for the industry.

Recently, however, the pulp and paper industry has faced very serious challenges. First, due to digital technology, there has been a steady decline in the need for pulp and paper products. The digital industry has continuously replaced printed products such as books, newspapers, and magazines. Second, there has been a trend initiated by developed countries to limit the use of wood as the raw material for the sake of environmental protection. This forces the industry to find a more efficient use of wood pulp as well as finding alternative, non-wood sources. Third, as an individual becomes wealthier and more conscious of health-care, the quality of a product becomes more important than the cost. Thus, a paradigm shift is needed from the cost-conscientious to the quality conscientious.

The objective of this article is to review the technologies aimed at engineering cellulose fibers for producing high-value added paper products.

Keywords: *Engineering cellulose fibers, bulk fiber, chemically cross-linked fibers, twisted fibers, nanocellulose, microcrystalline cellulose, nanofibrillated cellulose, drying, spray drying, flash drying, supercritical point drying*

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1. Introduction

Cellulose fibers have several distinctive advantages over other materials: abundant in nature, biodegradable, non-toxic, eco-friendly, sustainable, easy to fabricate, hydrophilic, and cost-effective. Cellulose fibers have been used to produce paper products, hygiene paper (e.g., tissue and towel), disposable absorbent products (e.g., diapers and sanitary pads), and as a raw material to produce a novel material such as nano-cellulose. The sources of the raw material are diverse. At present, wood has been most commonly used as the raw material. A recycled pulp from used products has been also used.

Recently, several significant changes have forced the pulp and paper industry to rethink their approach. First, due to digital technology, there has been a steady decline in the need for pulp and paper products. The digital industry has continuously replaced printed products such as books, newspapers, and magazines. Second, there has been a trend initiated by developed countries to limit the use of wood as the raw material for the sake of environmental protection. This forces the industry to find a more efficient use of wood pulp as well as finding alternative, non-wood sources. Third, as an individual becomes wealthier and more conscious of health-care, the quality of a product becomes more important than the cost. Thus, the pulp and paper industry has been under pressure to produce a superior product at a competitive cost. These changes have forced the pulp & industry to make the paradigm shift from being a low-cost producer to being a high quality producer.

The objective of this paper is to review the current status of the pulp and paper industry and to suggest the ways of engineering cellulose fibers from the raw materials to produce high-value added products.

2. Background

2.1 Raw materials for cellulose fibers

The major compositions of the raw materials are lignin, cellulose and hemicellulose. The raw material for producing a cellulose fiber, as known as a pulp, can either be a wood or non-wood. Woods have been the dominant raw materials for producing pulp. Recently, however, non-wood materials have been increasingly examined as alternatives to wood materials to protect forests and the environment.¹⁻³⁾ In particular, the biomass (i.e., solid waste) from oil palm trees and sugar cane bagasse has been used as the raw material.⁴⁻⁸⁾ Table 1 shows the source of the raw materials for producing cellulose fibers.

Table 1. Sources of raw materials

Sources	Species
Woods	
Softwoods	Pine, Douglas fir, Spruce
Hardwoods	Eucalyptus, Aspen, Birch
Non-woods	Bamboo, Kenaf, Sisal
Biomass of cellulosic materials	Oil palm trees, Sugar cane bagasse, Rice straw, Wheat straw
Recycled	—

2.2 Pulping

Pulping is a process of removing lignin for the raw materials. To date, wood has been predominantly used as the raw material. For chemical pulping, Kraft pulping and Sulfite pulping have been mainly used though the use of the latter has steadily declined due to environmental issues.¹⁾

In pulping, the term 'yield', is defined as the amount of the pulp obtained from the raw material, and it is expressed in %. As more non-cellulose components are removed from the raw material, the yield would decrease and would mean a lesser amount of pulp, but higher cellulose content would be obtained. With a higher content of the lignin, more vigorous pulping conditions (i.e., high con-

centration of pulping liquor, temperature, cooking time, *etc.*) would be required,

3. The structure of cellulose fibers: Multilamellar model

Bailey first published photomicrographs which showed that the cell wall of wood had a lamellar structure in 1983.⁹⁾ Since then, the multilamellar model has been generally accepted as the pore geometry of the cell wall proposed by Stone and Scallan.¹⁰⁾ Goring has speculated that the components (i.e., cellulose, hemicellulose, and lignin) are distributed in a multilamellar fashion as shown in Fig. 1.¹¹⁾

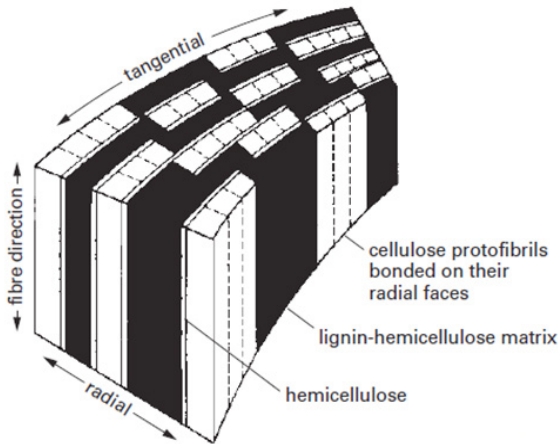


Fig. 1. Arrangements of cellulose, hemicellulose, and lignin in the wood cell wall prior to pulping.¹¹⁾

Then, as the lignin and the hemicellulose are progressively removed by a pulping process, pores are created where such components were previously located, as shown in Fig. 2. Thus, a pulp becomes highly porous after a complete removal of the lignin and its porosity should depend on the lignin and the hemicellulose contents. A never-been dried pulp after pulping becomes highly

porous. The pores created in the cell wall are referred to as the intra-pores (or intra-capillaries).^{10,11)} The water retention value has been used to determine the pore volume in the cell wall. Fig. 3 shows the cross-section of the cell wall of a spruce pulp fiber (as illustrated). It shows many pores in the cell wall, as well as the lumen.^{12,13)}

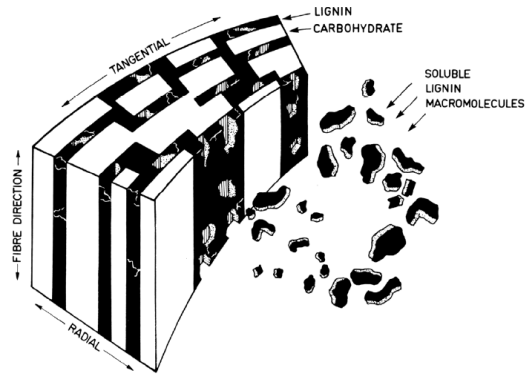


Fig. 2. Creation of the pores in the cell wall during pulping.



Fig. 3. The cross-section of the cell wall of a spruce pulp.¹²⁾

3.1 The multilamellar model for the pores in the cell wall

Stone and Scallan have proposed a laminar model of the pore in the cell wall.¹⁴⁻¹⁷⁾ As discussed earlier, the cell wall of a never-been dried pulp is highly porous, consisting of many (up to several hundred) lamellae. They are gradually collapsed during drying, resulting in the loss of the pores between them. Thus, the dried cell walls essen-

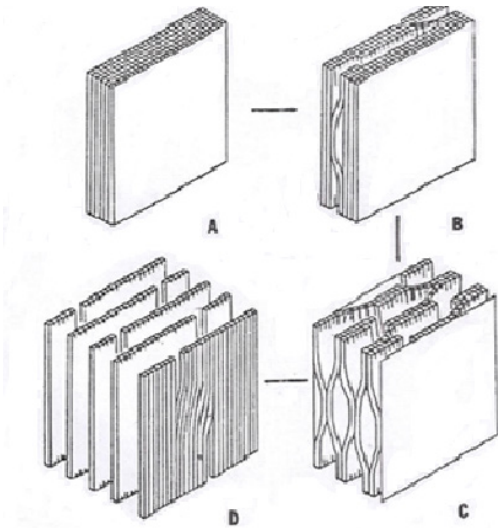


Fig. 4. The multilamellar model of the swollen cell wall.¹⁴⁾

tially become non-porous.

The collapsed cell wall may be reopened by subsequent reswelling in water. Fig. 4 shows the model of the swelling of the cell wall suggested by Stone and Scallan. It shows that the fully swollen cell wall should have a multilamellar pattern. It is important to realize that they would never be fully re-opened, resulting in the permanent collapse of some pores after drying. Namely, drying and reswelling of a pulp should be an irreversible process.

3.2 Pore structure

3.2.1 The surface tension theory (Campbell forces)

Campbell suggested that the surface tension force of water should be primarily responsible for the structural collapse of cellulose fibers.^{18,19)} The surface tension force is referred to as the Campbell force (or Campbell effect). The Campbell coefficient can be explained using the Laplace equation (Eq. 1).²⁰⁾

$$\Delta P_c = 2\tau \cos(\theta/w) \quad [1]$$

where, ΔP_c = the capillary pressure,

τ = the surface tension of liquid (i.e., water),

θ = the contact angle, and

w = the pore width.

Eq. 1 shows that ΔP_c should be proportional to the surface tension (τ) of a liquid. So, to reduce the surface tension of a drying liquid, several approaches have been taken.

A hydrocarbon liquid has much lower surface tension than water. It is, however, not miscible with water. Therefore, a direct replacement of water by a hydrocarbon solvent may not be possible. Merchant has developed the solvent exchange drying method (SED). For this method, a solvent which is miscible with both water and a hydrocarbon solvent is used as an intermediate. A polar solvent such as methanol or ethanol was used.²¹⁾

Freeze-drying from water has also tried to eliminate the surface tension force completely.^{15,21)} As another way of eliminating the surface tension force completely, critical point drying has been also tried with CO_2 as the final replacement solvent.^{22,23)} Since liquid CO_2 is not miscible with water, however, an intermediate solvent which is miscible with the two has been employed. As is the case with Merchant's solvent-exchange method, methanol or ethanol is used to this end.

The surface areas of the solvent-exchange dried pulps have been determined from the nitrogen adsorption experiments using the Brunauer-Emmett-Teller (BET) method.^{24,25)}

The results are summarized in Table 2 with the surface tension value of the final replacement solvent.

Fig. 5 is the plot of the BET surface area vs. the surface tension value of the final solvent from Table 2. Fig. 5 shows several interesting points.

Table 2. The BET surface area with the surface tension value of the final replacement solvent²¹⁾

Solvent	Surface tension (Dynes/cm)	BET area (m ² /g pulp)
Water	72.9	1.0
Water → MeOH	22.5	2.0 – 3.0
Water → MeOH →		
Benzene	28.9	43
Toluene	28.5	48
Cyclohexane	25.2	88
N-Hexane	18.4	108
N-Pentane	16.1	129
Freeze-dried from water	0	0 – 10
Critical-point dried (Water → MeOH → CO ₂)	0	0 – 10

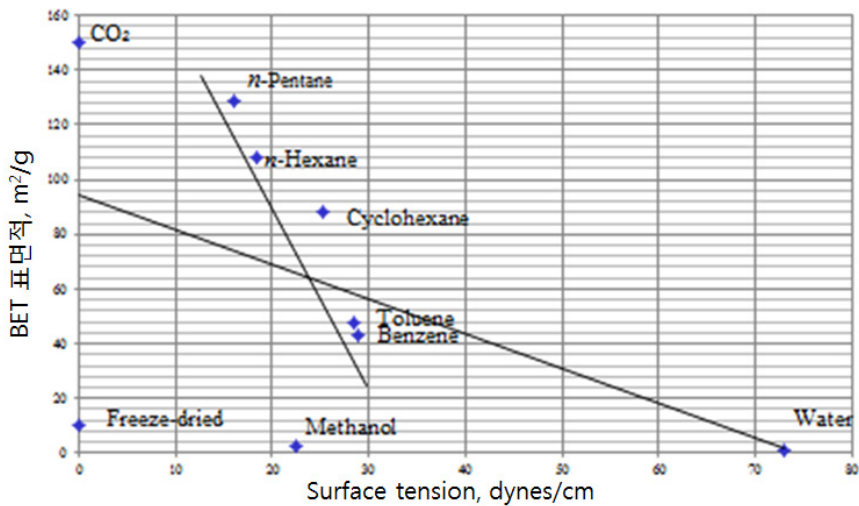


Fig. 5. BET surface area vs. surface tension of liquid.

First, the surface areas of the samples of the freeze-dried, from methanol, and from water, are very low. Second, the surface area of the critical point dried with CO₂ is largest, at about 150 m²/g. Third, the surface areas dried from a series of hydrocarbon liquids have a very high correlation with the surface tension values.

From these observations the following conclusions can be made regarding the solvent exchange methods.

1. The polarity of the final involved liquid is far more important than its surface tension

value in determining a degree of the pore collapse.

2. The surface tension theory may be applicable to non-polar liquids which have different surface tension values. In this case, there seems to be high correlation between the BET area and the surface tension value as shown in Fig. 5.
3. The reasons that the critical point drying with CO₂ are two-fold. One is that liquid CO₂ is non-polar and it is dried at zero-surface tension value. So, it eliminates both

the polarity and the Campbell forces simultaneously.

3.2.2 Solute exclusion technique

Stone and Scallan have developed the “solute-exclusion technique” to characterize the pores in the cell wall directly without drying.^{10,16,17,26)} The principle of the solute-exclusion technique is shown in Fig. 6. When a never-dried pulp is put in a polymer solution, polymer molecules will penetrate into the pores, depending on their molecular sizes. Then, some of the water in the pores will be replaced by such polymer molecules due to penetration. In this case, the water replaced is

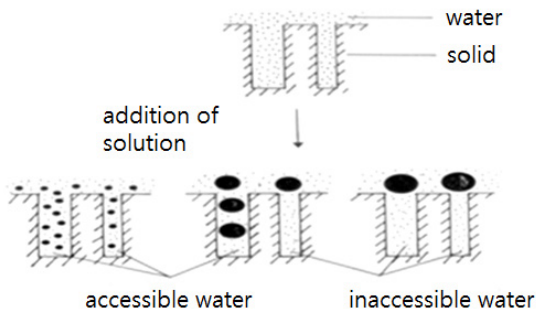


Fig. 6. The solute-exclusion technique by Stone and Scallan.¹⁰⁾

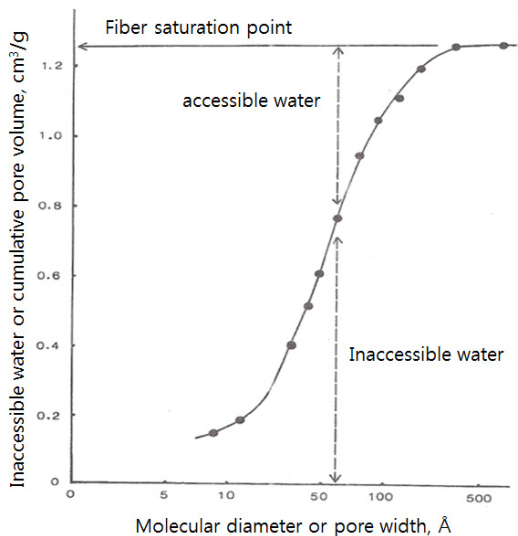


Fig. 7. Inaccessible water vs. pore width.²⁷⁾

called the accessible water to the polymer molecules; otherwise, it is the inaccessible water to the polymer molecules.

The accessible (or replaceable) water will dilute the polymer solution. Therefore, by measuring concentration changes in an initially known polymer solution, using a series of homologous polymers of different sizes, the amount of the accessible (or inaccessible) water can be determined. As polymers, a series of dextran polymers was most frequently used for this technique.

Fig. 7 shows a plot of the inaccessible water vs. molecular diameter (pore width) for a pulp fiber, obtained by the solute exclusion technique. Notice in the Fig. 7 that molecular diameter is plotted as log-scale.²⁷⁾

In the Fig. 7, the inaccessible water corresponds to the cumulative pore volume, while molecular diameter is equivalent to the pore width. Further, the fiber saturation point (FSP) is the total inaccessible water by the biggest polymer molecules. This FSP is empirically highly-correlated with the WRV (water retention volume of water) determined by the standard centrifugation method.²⁸⁾ This indicates that the WRV can be used as a measure of the total pore volume in the cell walls in the swollen state.

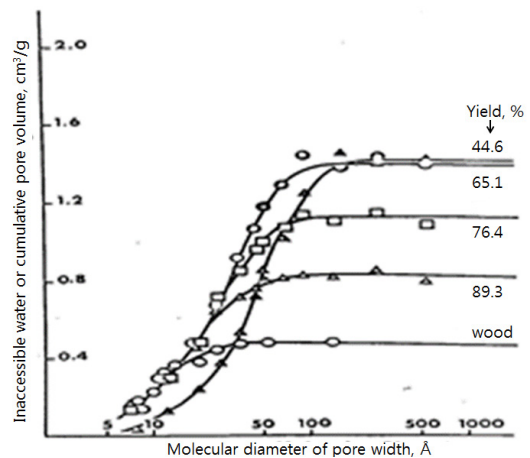


Fig. 8. Cumulative pore size distribution of the spruce Kraft pulp.²⁹⁾

Fig. 8 shows the cumulative pore volume (V_p) of various wood pulps having different yields. It shows V_p increases as the yield decreases (i.e., more lignin is removed) as expected. It shows also that the cell wall pores are quite broad in sizes ranging from about 10 Å to a several hundred Å.

3.2.3 Log-normal distribution model

It has been confirmed that the cumulative pore size distribution curves as shown in Fig. 8 should follow a log-normal frequency distribution mode by demonstrating the linearity between the two on a log-probability paper.²⁹⁻³¹ Fig. 9 are such plots of the curves in Fig. 8. In the plot, W_{med} is the pore width corresponding to the 50% of the cumulative pore volume, and σ is the standard deviation of the pore width where 84% of the cumulative pore size distribution is at the pore size of $W_{med} + \sigma$.³² Here, a cumulative frequency is the cumulative percentage of the pore volume normalized by the total pore volume, i.e., fiber saturation point.

Log-normal frequency distribution is expressed mathematically as follows,³²

$$f = \frac{1}{w \sigma \sqrt{2\pi}} \exp\left\{-\frac{[\ln(w) - \ln(W_{med})]^2}{2\sigma^2}\right\} \quad [2]$$

Eq. 2 shows that the two parameters of the median pore width (W_{med}) and the standard deviation (σ) are necessary to construct the frequency distribution curves as a function of pore width (w).

Fig. 10 shows the pore width frequency distribution constructed from Fig. 9. Eq. 2 indicates that the pore size distribution should be proportional to the pore width. Meanwhile, the actual pore size distribution follows a log-normal distribution, as shown in Fig. 11.³⁰

Allan and Ko have reasoned that a log-normal frequency distribution of the cell wall pores should be the combined effect of the forces involved during drying: 1) long-range van der Waals attraction forces to pull the laminates of the cell

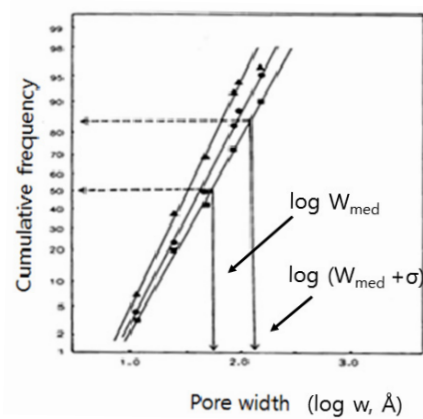


Fig. 9. Log-normal plot for a bleached pine sulfite.³¹

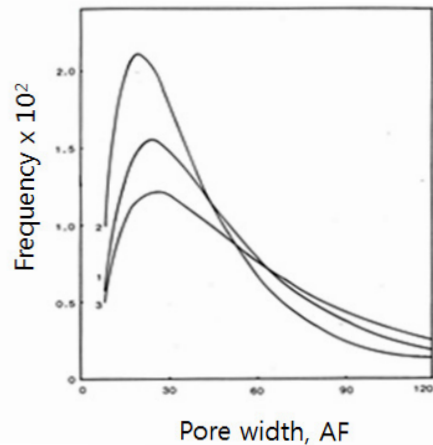


Fig. 10. Pore width frequency distribution of a bleached Pine sulfite pulp.³¹

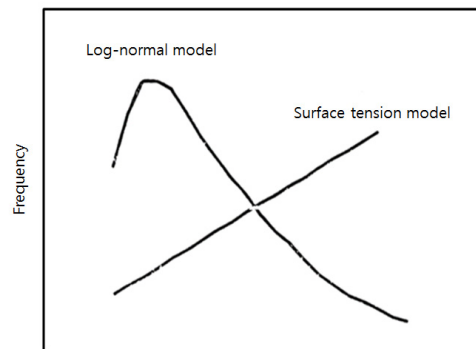


Fig. 11. Comparison of the pore size distribution between the surface tension model and log-normal model.³⁰

wall together, 2) electrical repulsion due to the overlap of the electrical double layers to push the laminates, and 3) the surface tension forces. Their theory is analogous to the DLVO (Derjagin-Landau-Verway-Overbeek) theory of the stability of colloidal.²⁰⁾

4. Engineering cellulose fibers for high value-added products

In this section, bulk fibers, carboxyl methyl cellulose (CMC) attachment technology, inclusion cellulose, nano and micro-cellulose, and drying of nano-cellulose will be discussed.

4.1 Bulk fibers

Bulk is defined as the volume per unit mass and has the unit of cm^3/g . Fiber bulk is inversely related to the coarseness which is the linear mass, expressed as miligrams per 100 m.¹²⁾ Thus, a higher coarseness means the heavier fiber. Bulk determines the strength, softness and absorbency. A high bulk may not be desirable for strength, but it is highly desirable for softness and absorbency of hygiene paper such as paper towels and disposable absorbent products like baby diapers and sanitary pads.

A high yield pulp is bulkier due to the lignin within. As the lignin is progressively removed, a pulp loses the bulk. Thus, a high yield pulp such as TMP (thermo-mechanical pulp) and CTMP (chemical thermo-mechanical pulp) has a much higher bulk than chemical pulp such as kraft or sulfate pulp.

For a good absorbency, a product requires a high absorbency capacity at a fast speed. To have a fast speed, cellulose fibers should have good wettability. A high yield pulp has, however, poor wettability due to the presence of lignin.³³⁾ Accordingly, a highly bleached chemical pulp such as Southern

softwood kraft pulp (SSK) has been used for highly absorbent products.

4.2 Chemically cross-linked fibers

The morphology of chemical pulp such as Softwood kraft pulp has a 2-dimensional flat morphology and has many internal pores which are fragile under the load. The fragility increases with the WRV.

So, there have been efforts to reduce the fragility of a pulp by permanently interlocking the pores by use of cross-linking chemicals. After the internal pores are cross-linked, the fiber will become bulky and stiff. For example, the Buckeye Cellulose Corp. developed the curly fibers by chemical cross-linking of a Foley pulp (Southern softwood kraft).³⁴⁻³⁸⁾

Chemical cross-linking in the cell walls will prevent the cell wall from swelling with water, resulting in a decrease of the WRV. Thus, an intensity of the chemical cross-linking may be estimated from the decrease in the WRV of the cross-linked fibers from that of the uncross-linked fibers by 20 - 60% reduction.³⁴⁾

One of the main issues in this chemical process is that chemical crosslinking occurs not only within the individual fibers, but also between the fibers to form the entangled forms. So, the chemical crosslinked fibers must be mechanically defibrated into individualized fibers known as "fluff". For defibration, a Waring blender or rotating disk refiner might be employed. A fluffing device may be also used such as one described elsewhere.³⁴⁻³⁸⁾

After chemical treatment, flash drying has been employed. It is observed that both dried and wet-fibers are twisted and curly. The average dry fiber twist count is in a range of 2.5 - 3.0 counts per millimeter whereas the average wet fiber twist count is at least approximately 1.5 - 2.0 counts per mm, less than the dry fiber twist count by 1.0 counts per mm.³⁴⁾

After flash drying, additional heat-treatment is required to cure the cross-linking, *i.e.*, to react with the cellulosic fibers. The rate and degree of cross-linking depends upon dryness of the fiber, temperature, pH, amount and type of catalyst and cross-linking agent and the method utilized for heating and/or drying the fibers while cross-linking is performed. Thus, the chemically cross-linked process invented by Buckeye Cellulose is a complicated process, dealing with cross-linking agents. Nonetheless, the fibers have been successfully used to produce disposable absorbent products such as baby diapers.

4.3 Twisted fibers by flash drying

Ko, et al. have developed a process of producing twisted fibers by the flash drying method without use of a chemical cross-linking agent.^{39,40} Flash drying is a well-known method for drying materials such as wood pulps, gypsum, starches, and inorganic fillers. It has been reported that flash drying should be more economical due to a lower capital cost and less manpower requirements than conventional drum drying.⁴¹

In flash drying, a never-dried pulp is exposed to a very hot drying air (or gas) environment for a very short time (up to less than a few seconds). These flash drying conditions are likely to put the fibers in a non-equilibrium state, thus making them shrink non-uniformly. Consequently, the flash dried fibers are likely to be twisted or coiled. In addition, such flash drying conditions may provide little time for the internal pores to be collapsed.^{39,40}

As an illustration, a never-been dried Kraft pulp has been flash-dried using a pilot flash dryer at the Barr-Rosin, Montreal, Canada, at the temperature of 232 – 327°C (or 450 – 620°F) for about one second. This temperature is much higher and the drying time is much shorter than that of conventional thermal drying, such as Yankee drying.

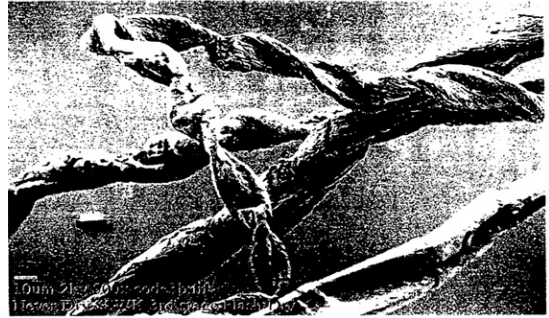


Fig. 12. Twisted, curly fibers produced by flash drying.³⁹⁾

Table 3. Comparison between the two bulk fibers methods

	Chemically -cross-linked	Flash dried
WRV, g/g Never-been dried	1.0	1.0
WRV reduction, %	60 – 80	No reduction, or increase
Crosslinking agent	Yes	No
Drying conditions		
Temp.	Less than 200°C	230°C or higher
Time	2 – 60minutes	– few seconds

Fig. 12 shows the twisted, curly fiber produced by flash drying method by Ko et al.³⁹⁾

Table 3 compares the chemical cross-linking method with the flash drying method. The WRV of a Foley fluff pulp is reported as about 1.0 g-water per g-pulp whereas its WRV after cross-linking reduces to around 0.2 – 0.4 g-water per g-pulp.³⁴⁾

4.4 CMC attachment technology by the STFI (Now Innventia), Stockholm, Sweden

Cellulose fibers are negatively charged. The total charge is referred to as the bulk charge which includes the charge inside and on the surface. The latter charge is called the surface charge. It is the

surface charge which is important in the wet-end chemistry and papermaking process. It influences strength (both dry and wet), retention of cationic additives such as dry strength resins, or debonders.

Unfortunately, however, the surface charge density of a pulp is too low for practical applications, so the effectiveness of such cationic additives is limited by the available surface charge density of the fiber. To compensate for this, for example, in paper towels, CMC (carboxyl methyl cellulose) is added to retain the wet strength agent which is cationic (Kymene-Hercules). To this end, an aqueous CMC solution and a cationic solution are added to a slurry of pulp.

A conventional way of increasing the negative charge density of a pulp has been by the means of chemical modifications such as carboxylation, methylation, and ethylation. All these chemical modifications are, however, costly and complex. It also can easily destroy the original structure. More importantly, however, such chemical modifications increase the total charge density (*i.e.*, bulk charge density) with a marginal increase in the surface charge density.

In a way to increase the surface charge density of cellulose fibers, Tom Lindstrom et al., have developed a method of attaching CMC (carboxyl methyl cellulose) to the surface of cellulose fibers without chemical reactions. They have identified the key variables that determine the retention efficiency of CMC to the fiber surfaces: 1) molecular weight (MW) and 2) the degree of the substitution, 3) temperature, 4) electrolytes and concentrations.⁴²⁻⁴⁵⁾

4.4.1 CMC specification

As discussed in the solute exclusion technique, a CMC of a high molecular weight (MW) should be more difficult to penetrate inside the fibers (*i.e.*, the cell wall pores). So, a high MW CMC is preferable to retain the CMC on the surface to increase the

surface charge density. It is reported that if the CMC has a MW higher than 1 million, it would not be able to penetrate into the cell wall pores resulting in a very little increase in the charge density.³⁵⁾ In addition, CMC should have a low degree of the substitution (DS = 0.52). For example, STFI has shown that, with a higher MW CMC (Finnfix WRH, MW = 1,000,000), the CMC retention was 96%, but with a lower MW CMC (Cekol FF2, MW = 280,000), the retention was only 59%.

4.4.2 Effect of temperature

It is found that a higher temperature is preferable for the retention of CMC by a pulp.³⁵⁾ Fig. 13 shows the effect of temperature on the attachment of CMC to a pulp. It shows clearly that the retention of the CMC is much higher at 120°C than at 80°C.

4.4.3 Surface charge density of CMC-attached cellulose fibers

Table 4 shows a comparison of charge density of the CMC-attached pulp with that of the untreated pulp.⁴²⁾ It shows that the untreated pulp has 3 unit (surface charge density) among the 40 total charge, occupying only 7.5%. Meanwhile, the CMC attached pulp has the surface charge of 29 among the total 67 charge, occupying 41.4%.

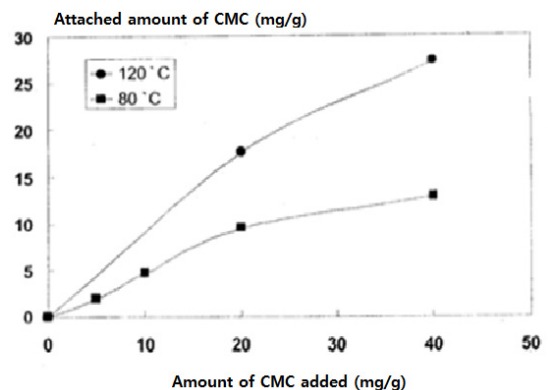


Fig. 13. Effect of temperature on CMC attachment to a wood pulp.⁴²⁾

Table 4. Internal and surface charge density of CMC attached pulp

CMC attached wood pulp			
* Furnish: Never-dried unbeaten ECF-bleached softwood kraft			
	Total	Surface	% of Surface charge
Reference (No treatment)	40	3	7.5
CMC attached	67	29	41.4

Source : T. Lindström, STFI, 2002.⁴²⁾

4.4.4 Water retention value

Beating (or refining) a pulp is commonly employed to increase the strength of a product made thereof. Beating increases the WRV (water retention value). The WRV has been determined using the method of SCAN-C 102XE, 15 min, at 3000 g.⁴²⁾ Fig. 14 shows the solid content vs. WRV of a beaten pulp and of CMC-attached pulp. In the Fig. 14, the WRV was determined by dividing the water content by the solid content. For example, if the solid content is 44%, then the water content would be 56%. So, the WRV would be 1.27 (56%/44%).

Fig. 14 shows that the WRV increases (solid content decreases) rapidly as the intensity of beating increases. Meanwhile, for the CMC attached pulp, the solid content remains constant though the WRV increases. This indicates the increase

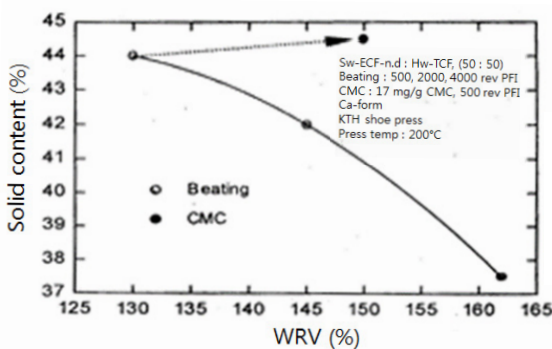


Fig. 14. Comparison of WRV of the CMC attached with the beating.

in the WRV primarily comes from the water held by the attached CMC, not from the swollen cell wall pores. Thus, the CMC would not contribute to swelling the cellulose fibers unlike the beating. It is suggested that an increase in WRV of the CMC-attached wood pulp will not negatively influence the drainage rate, dewatering and drying.

4.4.5 Wet strength enhancement by CMC attachment

A cellulose fiber has a very low surface charge density to interact with wet strength resin which is positively charged. For boxes or paper towels, PAE (Kymene) is commonly used with CMC.

Fig. 15 shows that wet strength of the hand-set constantly increases as the attached amount of CMC increases. On the other hand, the wet strength of the unattached pulp (control) is relatively low. This suggests the control pulp would require external CMC to increase the wet strength. (PAE - Kymene) which had been practiced in paper industry. The CMC attached pulp eliminates such necessity of adding CMC to retain PAE (Kymene). For CMC attachment, both NaCl and CaCl₂ electrolytes have been used. The figure shows that the effect of the electrolyte on the wet strength is negligible.

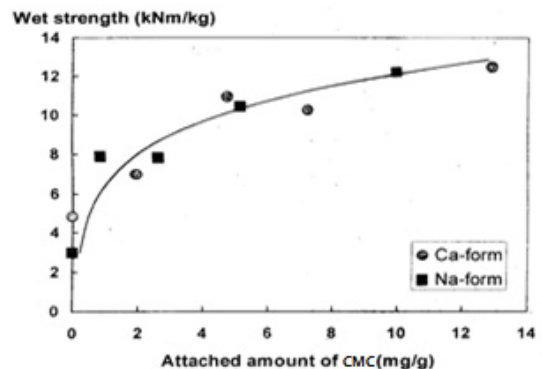


Fig. 15. Effect of CMC attachment on the wet strength (ECF-SW, PAE addition 5 mg/g).⁴²⁾

4.4.6 Stress-strain curves of CMC attached fibers

Fig. 16 shows the stress-strain curves of the handsheets made of the control (no CMC attachment) and those made of the CMC-attached pulp. It shows that the CMC-attachment provides much higher strength and the strain than the control (no attachment).

Beating is commonly used to increase the strength of a paper. Table 5 compares the effect on the stress-strain curves between beating and CMC attachment. It shows that the CMC-attached pulp may minimize beating process in increasing the strength of the product.

4.5 Inclusion cellulose

The internal pores in the lumen and the cell wall of cellulose fibers have been utilized as the storage for fluids and active ingredients.⁴⁶⁻⁴⁹ Inexpensive metal such as aluminum oxide (Al_2O_3) has been loaded into the lumen to increase the basis weight (BW) of a sheet to save more expensive cellulose fibers.⁴⁶ Active ingredient such as perfume, her-

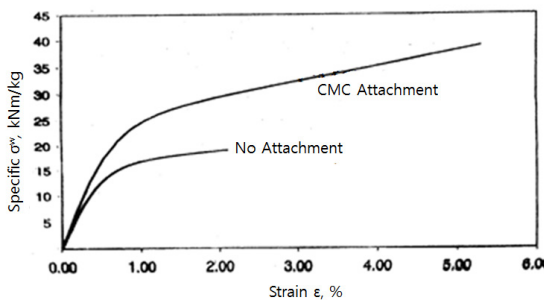


Fig. 16. Effect of CMC attachment (20 mg/g) on stress-strain curve.⁴²⁾

Table 5. Comparison between beating and CMC attachment⁴²⁾

	Tensile	Modules	Strain to failure	Bonding strength
Beating	++	++	+	+
CMC	++	(+)	++	++

bicide, pesticide, pharmaceuticals, and fertilizer were put into the cell wall pores. Then they were entrapped by closing the pores during drying. The active ingredient entrapped cellulose is referred to as “inclusion cellulose”. Once the ingredient entrapped, it may be difficult to be released from the inclusion cellulose. The closed pores may be opened by moisture to release the ingredient. So, inclusion cellulose is a way of producing as low-release system.

Since the swollen cell wall has the extremely large surface area of about 1000 m²/g, it may be used as the carrier for a catalyst to make ‘catalyst-inclusion cellulose’. Table 6 lists the materials loaded within cellulose for the inclusion cellulose.

Table 6. Materials loaded within cellulose (inclusion cellulose)⁴²⁾

Materials embedded within cellulose
• Inorganic pigments, white and colored
• Drugs, exemplified by aspirin
• Plant growth simulants
• Herbicides
• Fertilizers
• Simple sugars
• Glucose oligomers

4.6 Nano-Cellulose

Recently, nano-cellulose has attracted much interest in many industrial applications. Though nano-size is 1000 times smaller than micro-size, they are often used interchangeably to indicate the size is very small. Sometimes, micro- is used to indicate the aggregates of nano-size objects.⁴⁵⁾

Nanocellulose (NC) may be classified into:

- 1) Micro/Nano-crystalline cellulose (MCC/NCC)
- 2) Micro/Nano-fibrillated cellulose (MFC/MFC)

Table 7 lists some applications of nano-cellulose.

Table 7. Applications of nanocellulose

Bio-nanocomposites : electronics, automobilesa
Paper & paperboard applicationsa
- Dry strength agent
- Surface strength agent
- Nanocoatings / nanobarriers
Food applications : milk, ice cream, yogurt, etc.
Medical / pharmaceutical applications : tablet binder
Hygiene / absorbent products
Emulsion / dispersion applications : paints, etc.
Oil recovery applications

4.7 Microcrystalline Cellulose (MCC)

As shown in Fig. 1, cellulose fibers are comprised of the microfibrils which are the aggregates of the elementary fibrils. The elementary fibrils are comprised of the crystalline region and the non-crystalline region.^{45,46)}

In early 1960s, Battista invented on producing microcrystalline celluloses (MCC) by removing non-crystalline portions from the microfibrils in cellulose fibers. To this end, acid hydrolysis was employed to weaken the links between the crystalline portion and the non-crystalline portion. To liberate the crystalline portion from the acid-hydrolyzed pulp, a high shear force was applied.⁴⁷⁻⁵²⁾ To this end, a Gauline homogenizer or Microfluidizer may be used.^{47,53)} Avicel® from FMC (Food Manufacturing Company) is the representative brand name of the commercial microcrystalline cellulose.

It is realized that chemical treatment should be required to break the links between the crystalline portion and the non-crystalline portion. Mechanical treatment alone without chemical treatment will not work. For chemical treatment, acid such as hydrochloric acid or sulfuric acid may be employed.⁵⁴⁾

As acid treatment on the pulp proceeds, the pulp will be depolymerized until its degree of polymerization (DP) does not change any more, i.e., is

leveled-off. Battista has defined that DP as level-off degree polymerization (LODP).⁴⁸⁾ A LODP is found to depend on the source of raw material and the acid treatment conditions. It is observed that a LODP is highly correlated with the length (or size) of the crystallites. The higher the LODP is, the longer the crystal would be.^{47,48)}

It is, however, observed that the MCC in water forms aggregates and become very viscous even at a low consistency of 2 – 10%. To disintegrate the agglomerates into individual entities, ultrasonic treatment may be applied. The disintegrated crystallite aggregates has a wide distribution of sizes ranging from 40 to 250 or 300 microns and has a density of 1.2 to 1.57 g/cm³.⁴⁷⁾

Battista's work on MCC may be summarized as the following.

1. A mild acid-treatment step is necessary to eliminate the non-crystalline (amorphous) parts from, the elementary fibrils. Without the acid-treatment, it is impossible to produce nano-crystalline cellulose which has a high crystalline index. It is reported that the crystalline index of commercial MCC is about 78%.⁵⁴⁾
2. The LODP can be used as a measure of the length of the crystalline cellulose (crystallites). It depends on the source of cellulose material. The higher the LODP that the cellulose has, the longer the crystallites would be.
3. An aqueous NCC sol is dried to produce nano-crystallites. Spray drying has been used to this end. The nano-crystallites are, however, agglomerated to form large particles, by losing the original fibrous morphology. Once dried, it would be extremely difficult, if not impossible, to disintegrate the agglomerates into individual entities having the fibrous morphology. This is why Battista refers to the NCCF as the aggregates of microcrystalline celluloses (MCC).

4.8 Nano/Micro-fibrillated cellulose (N/MFC)

Microfibrillated cellulose (MFC) was first coined by Turbak, et al., to describe a product as a gel type material by passing wood pulp through a Gaulin type milk homogenizer at high temperature and high pressure.^{53,55-59} It is to be noted that producing MFC does not involve an acid-treatment step to eliminate non-crystalline region in contrast with producing microcrystalline cellulose (MCC). Accordingly, MCC should have always a higher crystalline index than MFC. It is to be noted that producing both MCC and MFC should require a device which generates high shearing forces such as a Gaulin homogenizer or microfluidizer.^{47,53}

5. Drying of nano-cellulose

5.1 Spray drying

Spray drying has been commonly used for an aqueous solution of hydrophilic particles. Battista et al., have employed the spray drying method for producing the aggregates of MCC. In spray drying, the size of the drops entering into the chamber plays an important role in determining the size of the product. Atomization is employed to produce smaller particles with minimal aggregation of the drops.⁴⁹ In addition, to minimize the aggregation during drying, a surfactant, or a protective colloid might be added to an aqueous solution.⁴⁷

The surface area of Avicel (Commercial) has only 2 m²/g, indicating the MCC particles are agglomerated during drying to form the large particles. This value is not much different from the dried pulp from water or methanol as shown in Table 2.

5.2 Supercritical point drying

Recently there have been attempts to apply the supercritical point drying method.⁶⁰⁻⁶³ Critical point drying has been commonly used to dehydrate bi-

ological tissue in the SEM (Scanning Electron Microscopy). The main purpose of critical point drying is to maintain the original morphology of the specimen by eliminating the surface tension of the fluid as discussed earlier as is the case with freeze drying. Freeze-drying has also been attempted to dry micro-fibrillated cellulose.⁶⁴ Supercritical drying has also been widely used to dry inorganic gel systems to create aerogels.⁶⁵

A liquid undergoes the three phases of the solid, the liquid, and the gas. At the critical conditions of the temperature and the pressure, however, a fluid has a state where the phase differences disappear. Such a state is referred to as the critical state, and the corresponding temperature and pressure is referred to as the critical temperature (T_c) and the critical pressure (P_c), respectively. A supercritical fluid (SCF) is any substance at a temperature and pressure above its critical point.

SCF is most widely used in extraction process such as the decaffeination of coffee and tea and extraction of flavors, fragrances, and essential oils from natural sources.⁶⁶ Such a process of extracting one component from another using SCF as the extracting solvent is referred to as supercritical fluid extraction (SFE). Supercritical fluid extraction has been used in the food industry.^{62,66-67}

As a supercritical fluid, CO₂ is most widely used since it is inexpensive, non-toxic and has favorable critical conditions of $T_c=31^\circ\text{C}$ and $P_c=74$ Bars.

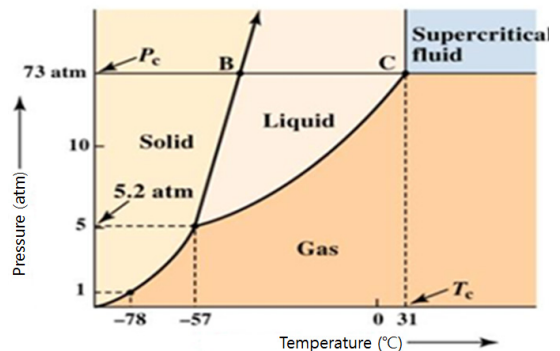


Fig. 17. Phase diagram for carbon dioxide.

Fig. 17 shows the phase diagram for carbon dioxide.

In the extraction process, solubility is an important factor. In order to increase the solubility of extractable ingredients in CO_2 , it is sometimes modified by co-solvents such as ethanol or methanol.^{62,68)}

Meanwhile, employing such co-solvents such as ethanol, methanol, or acetone can be detrimental for the supercritical point drying process. In other words, directly applying the supercritical extraction process for drying nano-crystalline cellulose fibers would work, but also affect adversely to produce NCCF as discussed in the following.

Brown et al., investigated the use of supercritical carbon dioxide (scCO_2) for the removal of moisture from cylindrical pieces of carrot. They found that carrots dried in the supercritical fluid environment were seen to retain their shape much better than air-dried carrots which underwent shrinkage. Samples dried in ethanol-modified scCO_2 possessed less dense structures and consequently displayed more favorable rehydrated textural properties than the air-dried equivalents.⁶²⁾

A supercritical point drying with CO_2 has been attempted for drying nano-cellulose. Since CO_2 is, however, not miscible with water, direct replacement of the water in the specimen by liquid CO_2 is impossible. Therefore, an intermediate fluid which is miscible with both water and liquid CO_2 needs to be introduced. As an intermediate fluid, a polar solvent such as methanol, ethanol, and acetone is generally used^{62, 64)} as a SPE process which was discussed earlier.

A literature survey reveals that this important fact has been frequently overlooked for supercritical point drying.

For example, Peng, et al., tried to use a supercritical point drying method with CO_2 in drying nano-fibrils.^{64,68)} Ethanol was used as an intermediate fluid between water and liquid CO_2 . But, they abandoned this method since it is practically

impossible to replace water with CO_2 using ethanol as an intermediate fluid.

Peng's work suggests that supercritical fluid such as ethanol or methanol used for the supercritical extraction process would not function well as an intermediate solvent for supercritical point drying. After giving up on using the supercritical point drying method, they reverted to the spray drying method as used by Battista, et al.

Thus, the use of polar liquid such as ethanol or methanol is a poor choice since it is practically impossible to replace water since the polar liquid and water are infinitely miscible. Besides, it should be noticed that such a polar solvent would not be much different from water in preventing the agglomeration of the particles as suggested in Table 2.

6. Conclusions

The pulp & paper industry has been considered as a mature industry whose market has been steadily declining. One characteristic of the mature industry has been to become a low-cost producer while less paying attention to developing a higher quality of the product. Consequently, there has not been much effort in engineering the raw material to produce a high-value added product or on developing the next generation of state-of-the art technology.

Recently, however, the pulp & paper industry has been forced to make the paradigm shift from the low-cost producer to the high-quality producer due to several reasons. First, the digital industry has penetrated into the pulp & paper industry by replacing paper products such as printed materials with online materials. Such replacement is expected to continue. Second, the woods have been the dominant raw material for the pulp & industry. The wood pulp producers, however, have

faced governmental regulations on using the trees for environmental protection. This has forced the industry to develop non-wood pulp as an alternative.

Drying hydrophilic material such as cellulose fibers while maintaining its original structure still remains a challenging problem.

Literature Cited

- Han, J. S., Properties of nonwood fibers, 1998 North American Nonwood Symposium, TAPPI, Atlanta, GA, USA, Feb. 17–18 (1998).
- Hurter, A. M., Utilization of annual plants and agricultural residues for the production of pulp and paper, 1998 Pulping Conference, TAPPI Press, Atlanta, GA, USA (1998).
- Rolf, B., Christina, J., Lars-Ake, L., and Yngve, L., Nonwood pulping technology present status and future, *IPPTA J.* 21(1):115–120 (2009).
- Hurter, R. W., Developments in pulp and paper manufacture from sugarcane bagasse, Symposium Workshop, Queensland University of Technology (QUT), Brisbane, Australia, May 3–4 (2007).
- Rodriguez, A., Sanchez, R., Eugenio, M. E., Yanez, R., and Jimenez, L., Soda-anthraquinone pulping of residues from oil palm industry, *Cellulose Chemistry and Technology* 44(7–8):239–248 (2010).
- Rushdan, I., Latifah, J., Hoi, W. K., and Mohd Nor, M. Y., Commercial-scale production of soda pulp and medium paper from oil palm empty fruit bunches, *J. Tropical Forest Sci.* 19(3):121–126 (2007).
- Wan Rosli, W. D. and Law, K.-N., Oil palm fibers as papermaking material: potentials and challenges, *BioResources* 6(1):901–917 (2011).
- Lee, J. S. and Shin, S. J., Chlorine dioxide bleaching properties of sugarcane bagasse pulp and oil palm trunk pulp, *Journal of Korea TAPPI* 47(4):13–20 (2015).
- Bailey, I. W., Cell wall structure of higher plants, *Industrial & Engineering Chemistry* 30(1):40–47 (1938).
- Stone, J. E. and Scallan, A. M., A structural models for the cell wall of water-swollen wood pulp fibers based on their accessibility to macromolecules, *Cellulose Chemistry and Technology* 2:343–358 (1968).
- Kerr, A. J. and Goring, D. A. I., The ultrastructural arrangement of the wood cell wall, *Cellulose Chemistry and Technology* 9(6):563–573 (1975).
- Mark, R. E. and Gillis, P. P., Chapter 10 Mechanical properties of fibers, In *Handbook of Physical and Mechanical Testing of Paper and Paperboard*, Vol. 1, Mark, R. E. (ed), Marcel Dekker, New York, USA (1983).
- McIntosh, D. C., The Effect of refining on the structure of the fiber wall, *Tappi J.* 50(10):482 (1967).
- Stone, J. E. and Scallan, A. M., A study of cell wall structure by nitrogen adsorption, *Pulp Paper Magazine Canada* 66:T407–T413 (1965).
- Stone, J. E., Scallan, A. M., and Aberson, G. M. A., Wall density of native cellulose fibers, *Pulp Paper Magazine Canada* 67(5):T263–T268 (1966).
- Stone, J. E., Treiber, E., and Abrahamson, B., Accessibility of regenerated cellulose to solute molecules of molecular weight of 180 to 2×10^6 , *Tappi J.* 52:108–110 (1969).
- Stone, J. E., Scallan, A. M., and ad Abrahamson, B., Influence of beating on cell wall swelling and internal fibrillation, *Svensk Papperstidn.* 71:687–694 (1968).
- Campbell, W. B., A physical theory of the beating process, *Paper Trade J.* 95(8):29–33 (1932).

19. Campbell, W. B., Hydration and beating of cellulose pulps, *Industrial & Engineering Chemistry* 26:218–219 (1934).
20. Hiemenz, P.C., *Principles of Colloid and Surface Chemistry*, 2nd ed., Marcel Dekker, Inc., New York, USA, pp. 296–302 (1986).
21. Merchant, M. V., A study of water-swollen cellulose fibers which have been liquid-exchanged and dried from hydrocarbons, *Tappi J.* 40(9):771–781 (1957).
22. Sommers, R. A., A surface-area study of cotton dried from liquid carbon dioxide at zero surface tension, *Tappi J.* 46:562–569 (1963).
23. Weatherwax, R. C., Collapse of cell-wall pores during drying of cellulose, *J. Colloid Interface Science* 62:432–446 (1977).
24. Brunauer, S., Emmett, P. H., and Teller, E., Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.*, 60(2):309–319 (1938).
25. Brunauer, S., *The Adsorption of Gases and Vapors*, Vol. I, Physical Adsorption, Princeton University, Princeton, New York, USA (1943).
26. Stone, J. E., Scallan, A. M., and Abrahamson, B., Technical Report No. 538, Pulp & Paper Research Institute of Canada, Pointe Claire, P.Q., Canada (1968).
27. Stone, J. E., Scallan, A. M., Donefer, E., and Ahlgren, P. E. V., *Pulp and Paper Reports*, No. 11, Pulp and Paper Research Institute of Canada, Pointe Claire, P.Q., Canada (1968).
28. Stone, J. E. and Scallan, A. M., Effect of component removal upon the porous swelling in water and fiber saturation point, *Tappi J.* 50(10):496–501 (1967).
29. Ahlgren, P. A. V., Chlorite delignification of spruce wood, Ph.D. Dissertation, McGill University, Montreal, P.Q., Canada (1970).
30. Allan, G. G. and Ko, Y. C., The microporosity of pulp: The forces influencing the intra- and inter-fiber pore structure and pore size distribution, *Cellulose Chemistry and Technology* 29(4):479–485 (1995).
31. Ko, Y. C., *The Characterization of the Pores within Cellulose Fibers*, Ph.D. Dissertation, University of Washington, Seattle, Washington (1981).
32. Bury, K. V., *Statistical Models in Applied Science*, John Wiley & Sons, New York, pp. 278–298 (1975).
33. Draper, E., *The Effect of Single Fiber Properties and Structure on Absorbency*, Master's Thesis, Paper Science and Engineering, University of Washington, Seattle, Washington (2003).
34. Moore, D. R., Owens, J. R., and Schoggen, H. L., Twisted, chemically stiffened cellulosic fibers and absorbent structures made therefrom, US Patent No. 4898642, Feb. 6 (1990).
35. Herron, C. M., Dean, W. L., Moore, D. R., Owens, J. W., and Schoggen, H. L., Process for making individualized, crosslinked fibers having reduced residuals and fibers thereof, US Patent No. 4889595, Dec. 26 (1989).
36. Dean, W. L., Moore, D. R., Owens, J. W., and Schoggen, H. L., Absorbent structure containing individualized, crosslinked fibers, US Patent No. 4822453, April 18 (1989).
37. Cook, J. T., Lash, G. R., Moore, D. R., and Young, G. A., Absorbent structures containing stiffened fibers and superabsorbent material, Assignee: P&G., US Patent No. 5,360,420, Nov. 1 (1994).
38. Dean, W. L., Moore, D. R., Owens, J. W., Schoggen, H. L., Bourbon, R. M., and Cook, J. T., Individualized crosslinked fibers and process for making said fibers, US Patent No. 4888093, Dec. 19 (1989).
39. Ko, Y. C., Hu, S. H., and Makoui, K. B., Wood pulp fiber morphology modifications through thermal drying, US Patent No. 6,837,970, Jan. 4 (2005).
40. Hu, S. H. and Ko, Y. C., Method of producing

- twisted, curly fibers, US Patent No. 6,984,447, Jan, 10 (2006).
41. Enstroem, H. E., Hovstad, O. B., and Ivnas, L., Flash drying system for pulp - design factors, *Pulp & Paper*, Part 1, (4 pages), Aug. 21 & Aug. 28 (1967).
 42. Laine, J., Lindstrom, T., Glad Nordmark, G., and Risinger, G., Studies on topochemical modification of cellulosic fibres, Part 3, The effect of carboxymethyl cellulose attachment on wet-strength development by alkaline-curing polyamide-amine epichlorohydrin resins, *Nordic Pulp Paper Res. J.* 17(1):57-60 (2002).
 43. Laine, J. and Lindstrom, T., The effect of carboxymethyl cellulose attachment on fibre swelling and paper strength, *Nordic Pulp Paper Res. J.* 17(1):50-56 (2002).
 44. Laine, J., Lindstrom, T., Glad-Nordmark, G., and Risinger, G., Studies on topochemical modification of cellulose onto fibres, *Nordic Pulp and Paper Res. J.* 15(5):520-526 (2000).
 45. Glad-Nordmark, G., Laine, J., Lindström, T., and Risinger, G., Method for modifying cellulose-based fiber material, Patent WO2001021890 A1, March 29 (2001).
 46. Allan, G. G., Carroll, J. P., Negri, A. R., Raghuraman, P., Ritzenthaler, P., and Yahiaoui, A., The microporosity of pulp: The precipitation of inorganic fillers within the micropores of the cell wall, *Tappi J.* 75(1):175-178 (1992).
 47. Allan, G. G., Controlled release composition and method for using, US Patent No. 5,252,242, Oct. 12 (1993).
 48. Allan, G. G., Carroll, J. P., Ko, Y. C., Lee, A. W. W., Negri, A. R., and Ritzenthaler, P., New technologies based on the microporosity of cellulosic pulp fibers, *Japan Tappi J.* 45(9):986-992 (1991).
 49. Allan, G. G. and Ko, Y., Method for preparing a controlled release composition, US Patent No. 4,388,352, June 14 (1983).
 50. Chinga-Carrasco, G., Cellulose fibers, nanofibrils and microfibrils: the morphological sequence of MFC components from a plant physiology and fiber technology point of view, *Nanoscale Res. Lett.* 6(1):417 (2011).
 51. Meier, H., Chemical and morphological aspects of the fine structure of wood, *Pure and Applied Chemistry* 5:37-52 (1962).
 52. Battista, O. A., *Microcrystal Polymer Science*, McGraw-Hill, New York (1975).
 53. Battista, O. A. and Smith, P. A., Level-off D.P. Cellulose Products, US Patent No. 2,978,446 (1961).
 54. Battista, O. A. and Smith, P. A., Formed products of cellulose crystallite aggregates, US Patent No. 3,278,519 (1966).
 55. Battista, O. A., Food compositions in incorporating cellulose crystalline aggregates, US Patent No. 3,023,104 (1962).
 56. Battista, O. A., Manufacture of pharmaceutical preparations containing cellulose crystallite aggregates, US Patent No. 3,146,168 (1964).
 57. Battista, O. A., Hydrolysis and crystallization of cellulose, *Industrial Engineering & Chemistry* 42(3):503-507 (1950).
 58. Ankerfors, M. and Lindström, T., Method for providing nanocellulose comprising modified cellulose fibers, Patent WO2009126106 A1 (2009).
 59. Vanhatalo, K. M. and Dahl, O. P., Effect of mild hydrolysis parameters on properties of microcrystalline cellulose, *BioResources* 9(3):4729-4740 (2014).
 60. Turbak, A. F., Snyder, F. W., and Sandberg, K. R., Food products containing microfibrillated cellulose, US Patent No. 4,341,807, Jul. 27 (1982).
 61. Turbak, A. F., Snyder, F. W., and Sandberg, K. R., Microfibrillated Cellulose, US Patent No. 4,374,702, Feb. 22 (1983).

62. Turbak, A. F., Snyder, F. W., and Sandberg, K. R., Suspensions containing microfibrillated cellulose, US Patent No. 4,378,381, Mar. 29 (1983).
63. Turbak, A. F., Snyder, F. W., and Sandberg, K. R., Suspensions containing microfibrillated cellulose, US Patent No. 4,500,546, Feb. 19 (1985).
64. Turbak, A. F., Snyder, F. W., and Sandberg, K. R., Microfibrillated cellulose, a new cellulose product: Properties, uses and commercial potential, In Proceedings of the Ninth Cellulose Conference, Sarko, A. (ed.), Applied Polymer Symposia 37, Wiley, New York, pp. 815–827 (1983).
65. Gardner, D. J., Han, Y., and Peng Y., Method for drying cellulose nanofibrils, US Patent No. 8,372,320, Feb. 12 (2013).
66. Brown, Z. K., The Drying of Foods using Supercritical Carbon Dioxide, Ph.D. Thesis, University of Birmingham (2010).
67. Horne, J. E., Automatic critical point drying apparatus, US Patent No. 4,055,904, Nov. 1 (1977).
68. Peng, Y., Gardner, D. J., and Han, Y., Drying cellulose nanofibrils: In search of a suitable method, Cellulose 19(1):91–102 (2012).
69. Oevreboe, H. H., Wichmann, J. U., Opstad, A., and Holtan, S., Method of drying microfibrillated cellulose, US Patent No. 2012/0090192 A1, Apr. 19 (2012).
70. Rangarajan, B. and Lira, C. T., Production of aerogels, J. of Supercritical Fluids 4(10):1–6 (1991).
71. Reverchon, E., Supercritical fluid extraction and fractionation of essential oils and related products, J. of Supercritical Fluids 10(1):1–37 (1997).
72. Brunner, G., Supercritical fluids: Technology and application to food processing, J. of Food Engineering 67(1–2):21–33 (2005).
73. Peng, B. L., Dhar, N., Liu, H. L., and Tam, K. C., Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective, Canadian J. of Chemical Engineering 89(5):1191–1206 (2011).