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Chemically Enhanced Water Removal in Papermaking

James John Beaupré

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CHEMICALLY ENHANCED WATER REMOVAL IN PAPERMAKING

By

James John Beaupré

B.Sc. University of Maine, 2007

A DISSERTATION

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Doctor of Philosophy

(in Chemical Engineering)

The Graduate School

The University of Maine

May 2012

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CHEMICALLY ENHANCED WATER REMOVAL IN PAPERMAKING

By James John Beaupré

Thesis Advisor: Dr. David J. Neivandt

An Abstract of the Dissertation Presented
in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy
(in Chemical Engineering)
May 2012

This work examines the utilization of chemical means to enhance the amount of water removed in the papermaking process prior to the application of heat. Through wet end application of a cationic surfactant, a significant increase in the amount of water removed in the forming and pressing sections is observed. This results in a reduction in the energy required to thoroughly dry the paper.

A variety of compounds hypothesized to potentially enhance dewatering were examined. A cationic surfactant, cetyltrimethylammonium bromide (CTAB), produced significant enhanced dewatering via addition to a pulp slurry. Extensive bench top testing characterized the extent of reduction of water retention of a fiber mat in the presence of CTAB after being exposed to drainage and pressing operations. The addition of CTAB favorably altered the pore structure of the fiber mat and promoted dewatering. The laboratory work was successfully translated to the pilot scale. The addition of CTAB resulted in an increase in the rate of production of paper by 18%. Post trial analysis indicated that an additional 12% production increase may have been available that was unrealized during the pilot scale run. While the addition of CTAB had a dramatic affect on dewatering, several

potentially negative effects were identified. Specifically, the fiber surface was shown to be charge reversed from negative to positive, the surface tension of the slurry was significantly reduced, the fiber sheet was considerably thicker, and the sheet strength was reduced by the addition of CTAB. Efforts to mitigate the negative effects observed in both the laboratory and pilot scale testing determined that the addition of an anionic clay reversed the bulking, charge, and surface tension effects, however it failed to recover the strength loss.

In conclusion, the work demonstrated that the addition of the cationic surfactant CTAB to a pulp slurry results in significant chemically enhanced water removal. The technology is expected to have direct application in niche markets which do not base product quality on strength or bulking. Additional implementation of the technology may be possible with further evaluation.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1. Description of the Problem

Over the past 200 years papermaking has gone from an art to a science with many technological improvements aimed at making better paper less expensive and more efficiently. Due to the nature of the papermaking process, the largest improvements in dewatering have been mechanical, such as increases in the size of machines for greater production and the implementation of new machine designs. In the past twenty years the North American papermaking industry has encountered a great deal of competition from growing papermaking industries in South America, Asia, and Europe where significant amounts of capital have been invested in building larger, faster machines. These new high speed machines leave aging paper manufacturing facilities in a highly competitive environment while facing high labor and energy costs and using significantly older, slower machines. In order to survive, papermakers have leveraged their ingenuity to develop unique types of paper to carve out niche markets and apply as much efficiency to the current installed machines as possible. However this has not been enough to make up for the lack of ability to compete with the newer production methods and newer machines worldwide which allow for lower cost production.

The formation of a sheet of paper from a pulp slurry comprised of wood fibers requires three steps to produce a finished sheet of paper. These steps are; the

removal of water by wet end drainage, pressing, and drying, each step attributes a higher cost to the process, respectively. There has been much work conducted in exploring mechanical means of increasing removal of water prior to applying heat in order to reduce the amount of energy required for the drying process. Less water left in the sheet translates into decreased energy expenditure, or a greater level of production with the equivalent energy cost. However, very little attention has been paid to chemical enhancements in drainage, pressing, and drying. As paper machines age and speed requirements increase, machines tend to become “dryer limited.” When a machine is dryer limited, its rate of production is limited by the rate at which water can be removed by the application of heat. It is generally impractical and economically unfeasible to install the capital equipment needed to overcome this limitation. Therefore, improvements in increasing water removal efficiency prior to heat application are at the forefront of development.

1.2. Components of the Paper Machine

The formation of a sheet of paper from a pulp slurry requires three unit operations to produce a finished product. These three operations are; forming operations, pressing operations, and drying operations as shown in Figure 1.1.

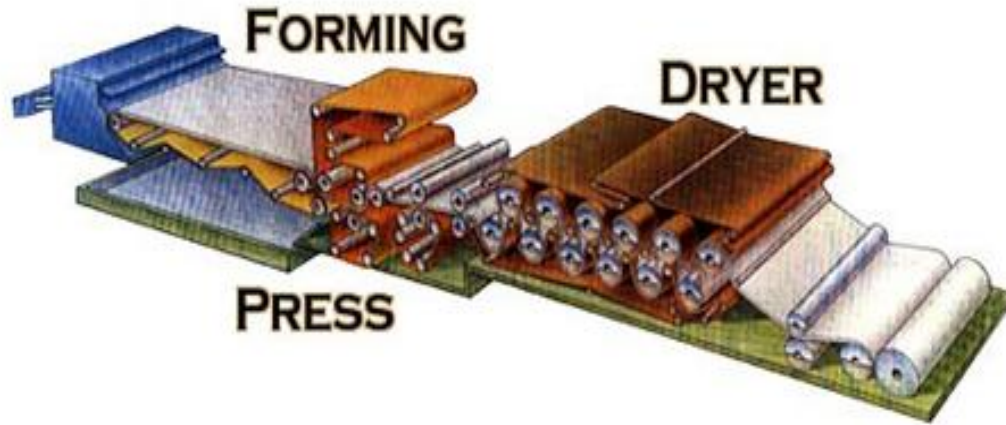


Figure 1.1. Example of a Fourdrinier paper machine. (www.tappi.com)

In the forming section the initial dewatering of the fiber mat commences. The pulp slurry is generally ~0.5% fiber and filler and ~99.5% water when it begins the sheet formation process. Water is removed by generating a pressure gradient across the mat. This pressure gradient is created by placing stationary hydrodynamic foils underneath the forming fabric. The forming fabric provides the initial stability of the newly formed sheet. The speed of the sheet over the hydrodynamic foils results in a pressure drop behind the foil due to Bernoulli's principle. As the sheet progresses down the forming section, the hydrodynamic foils are assisted by the addition of vacuum boxes to further dewater the sheet. At the end of the forming section the sheet enters the pressing section at approximately 20% solids depending upon the basis weight of the sheet, (heavier sheets will be wetter) (Smook 2002).

Pressing, as a unit operation in paper making, has two functions; to remove water from the sheet, and to compress the wet fibrous web so that fiber-fiber hydrogen bonding can begin to occur. Pressing continues the dewatering process that began in the forming section. The press nip, where the dewatering of the sheet

occurs due to a pressure pulse, is located between two press rolls. Of these two rolls, one is covered with rubber and the second is either a steel or composite covered roll. The sheet is transferred from the forming section fabric to the press section felts which serve two purposes; to provide support for the sheet which cannot yet support its own weight, and to assist in carrying excess water from the sheet. The sheet leaves the press section at approximately 40% - 50% solids (Smook 2002).

Smook (2002) states that the dryer section of a paper machine is the most expensive portion of the machine to build in terms of the capital cost of the equipment, and installation. Further, the dryer section has the greatest operational cost due to the high energy consumption required to evaporate the remaining water from the sheet. The moisture content of the final product is generally accepted to be ~5%. Smook concludes that due to the overall cost of the dryer section, improvements to increase the evaporation rate and reduce energy usage are well justified. Often the drying operation receives less attention and opportunities to improve this section's efficiency are overlooked. The sheet enters the dryer section at typically 50% to 60% moisture and passes over steam heated rolls to apply energy for drying. Drying may also be accomplished by steam heat in dryer cans, infrared dryers, natural gas dryers or a combination of two of these methods. Dryer felts in two tier steam dryers are used to initially aid in supporting the sheet and, later, in the dryer section to hold the sheet tightly to the steam heated rolls to maximize heat transfer.

1.3. Cellulose and Fiber Structure

The structure and chemical properties of cellulose fibers are topics which have been reviewed and studied thoroughly (e.g.: Côté Jr 1967, Butterfield 1980, and Sjostrom 1993). Sjostrom depicts a wood cell as an assembly of cellulose chains forming a framework that is encompassed by a hemicellulose matrix, and lignin, which serves as an adhesive. Cellulose fibrils, which are smaller cellulose frameworks that combine to create cell walls, adhere to each other through hydrogen bonding. These fibrils assemble to create wood cells consisting of several cell wall layers. Wood fibers are comprised of wood cells that consist largely of cellulose, lignin, and hemicelluloses (Sjostrom 1993).

1.3.1. Ultra Structure of the Cell Wall

The wood cell wall is built in four distinct layers: the primary wall and three layers of the secondary wall (Côté 1967). The cell wall with a thin film, the warty layer, surrounds a hollow center, the lumen. Individual cells are held together by lignin which is found within the cell wall as well as in the middle lamella. The middle lamella is a conglomeration of hemicelluloses and lignin located between cells. The primary wall encompasses the secondary wall and separates it from the middle lamella as shown in Figure 1.2.

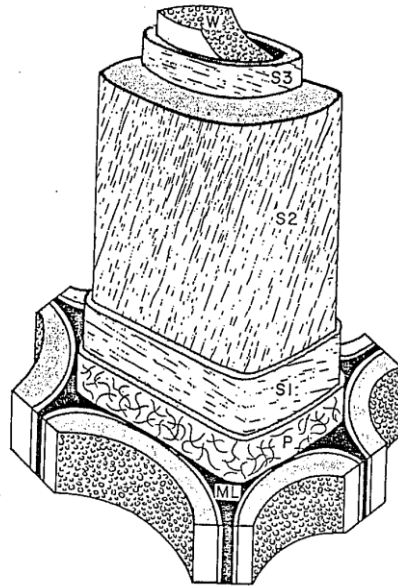


Figure 1.2: Structure of a woody cell depicting the middle lamella (ML), primary wall (P), the three layers of the secondary wall (S1, S2, and S3), and the warty layer (W). (Côté 1967)

The secondary layer makes up the majority of the cell wall. To enter the lumen, which is the empty cavity at the center of the fiber, molecules must travel, by diffusion, through the cell wall or through larger holes that connect the outside of the cell to the interior (pits) (Sjostrom 1993). Pits allow for the transport of water in the radial direction of the tree structure by connecting adjacent cells to each other through the middle lamellae. As the cell is being pulped in the papermaking process, the pits allow for the impregnation of the fiber with various additives used in the papermaking industry. In most pulping processes the middle lamella is destroyed and carried out by the pulping liquors from the resulting wood pulp.

1.3.2. Distribution of Lignin and Cellulose

When examining wood fiber on a molecular scale the most abundant constituent is cellulose comprising 50 to 70wt% of the total fiber content. Lignin

makes up 25 to 45wt% of the fiber, with the remaining portion of the fiber being hemicelluloses and other wood polysaccharides. The majority of the lignin is found within the cell wall, with the surface of the fiber primarily comprising cellulose (Sjostrom 1993). Cellulose consists of polymerized β -D-glucopyranoses in the 4C1 chair conformation which are joined by β 1-4 glycosidic linkages (Sjostrom 1993). The linked chains are bound together through hydrogen bonding creating microfibrils which in turn form the walls of the cellulose fiber structure. The abundance of hydroxyl groups creates many locations for hydrogen bonding as is shown below in Figure 1.3.

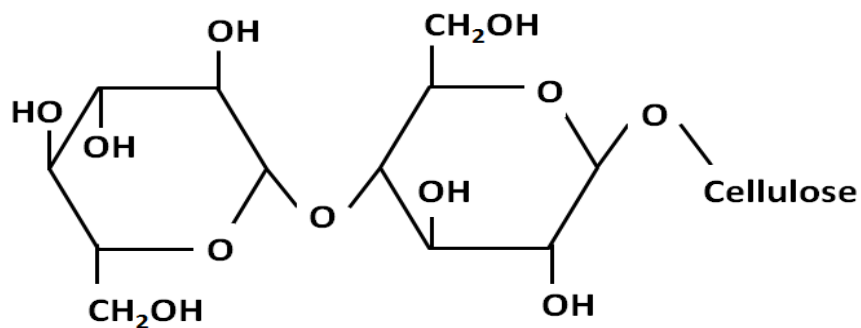


Figure 1.3. Cellulose structure depicting β -D-glucopyranose chain unit.

Hydrogen bonding facilitates interfiber bonding and enhances the formation of products such as paper, providing their core strength. This versatile chemical framework also permits ample opportunity to apply surface treatments in industrial production to affect various properties such as brightness and strength (Smook 2002).

1.4. Wood Pulping Properties

Wood pulping is the process by which raw wood is reduced to a slurry of wood fibers. This is accomplished by methodically destroying the bonds that hold

the wood together, which may be achieved by chemical means, mechanical means, or a combination of the two (Smook 2002). Wood pulp is generally comprised of the three major components carried over from the cellulose fibers, namely: cellulose, lignin, and hemicelluloses. Pulping processes generally form an abundance of carboxylic acid groups on the cellulose chains resulting in a negative surface charge. Different methods of pulping produce different quality pulps that contain varying proportions of the three wood cell components. Chemical pulps make up the largest proportion of pulp production in North America, the most common type is a wood pulp produced by the kraft pulping process. Chemical pulping dissolves the middle lamella that holds the wood cells together. This represents a drawback in the chemical pulping process, as the chemistry that dissolves the bonds holding the cells together also dissolves and reacts away portions of the cellulose fiber, leading to lower pulp yields. The majority of lignin left in the chemical pulping processes is found within the cell walls. This residual lignin does not affect the ability of the fiber surface to hydrogen bond with adjacent fibers. A greater number of hydrogen bonds between adjacent fibers produce a stronger final product for kraft pulps, compared to mechanical pulping methods. Mechanical pulping produces a pulp that has a higher lignin content than chemical pulps due to the fact that mechanical pulping physically ruptures bonds between wood cells to create a fibrous mass. The lignin is left mostly intact in portions of the middle lamella on the resulting fibers. This residual lignin is then partially bleached and washed off (Gullichsen 1999). Pulps with larger amounts of residual lignin tend to form weaker products due to

non-uniformity in hydrogen bond distribution and are thus considered lower quality pulps (Smook 2002).

1.5. Sheet Solids Limitations

Paper machine furnishes are blended with pulps from various sources to optimize the running conditions of each machine and to meet specifications of the given type of paper being produced. However, as paper machines age and speed requirements increase, the machines tend to become “dryer limited” regardless of the machine furnish. When a machine is dryer limited, its rate of production is limited by the rate at which water can be removed in the dryer section. Further speed increases would produce a sheet that would have higher than acceptable moisture levels. It is impractical and economically unfeasible to install a longer dryer section to overcome this limitation. Therefore, improvements in increasing water removal efficiency are typically concentrated on the forming section and press section. Advancements in these two sections to date have been solely mechanical. Theoretically, a higher dryness coming from the forming section into the press section should generate a higher dryness exiting the press section. However in reality most machines cannot realize this enhancement due to the level of pressing required to remove the remaining water from the sheet. That is, the pressures generally required to remove water in the press section to a level greater than a given value results in crushing of the sheet, thereby damaging the final product. As such increased amounts of dewatering in the forming section do not generally translate to increased solids exiting the press section; rather the sheet is

pressed to the maximum value possible without structural damage. It is this pressure that governs the water removal rate, and hence the exiting solids content. However, methodologies have been developed that result in higher solids exiting the press section by mechanical means other than increasing the pressure applied to the sheet.

CHAPTER 2

LITERATURE REVIEW

2.1. Distribution of Water in Cellulose and Cellulose Fiber Mats

Previous work has shown that water in a pulp slurry exists in the vicinity of cellulose fibers as unbound water, freezing-bound water, and nonfreezing-bound water (Park 2007). The unbound water is water that is removed in the papermaking process by dewatering the sheet via free drainage, pressure, and heat; such water has a freezing temperature consistent with that of bulk water (0°C). The bound water, both freezing and nonfreezing, neighbors the fiber surface. The nonfreezing-bound water is defined as the few layers of water adjacent to the fiber surface that due to the strong interfacial interaction are unable to undergo the conformational rearrangements necessary to freeze; that is, these water molecules have no freezing temperature. The freezing-bound water is water which is bound to the nonfreezing-bound water and is adjacent to the bulk fluid (Park 2007). Freezing-bound water has a depressed freezing point due to its proximity to the nonfreezing-bound water (Park 2007). Further work by Park et al. (2007), has compartmentalized these types of water by differential scanning calorimetry and thermogravimetric analysis into two categories, easy-to-remove water and hard-to-remove water. Easy-to-remove water is considered free water and contains nearly all of the available unbound water (~75% of the unbound water). Hard-to-remove water includes trapped unbound water within the fiber walls (~25% of the total

unbound water) as well as all of the freezing and nonfreezing-bound waters (Park 2007). Park et al. (2007) have shown that that hard-to-remove water accounts for 30 to 60% of the total water remaining in the sheet after pressing.

2.2. Drainage and Formation

In order to understand the complete dewatering phenomenon, it must be analyzed from the beginning of the papermaking process. Stock preparation stage is the first stage of the papermaking process, this portion of the process is also known as the wet end. In stock preparation, wood fibers are mixed with water, fillers, and additives. From stock preparation the pulp slurry is transported to the headbox of a paper machine. The structure of a headbox in a modern paper machine is depicted in Figure 2.1.

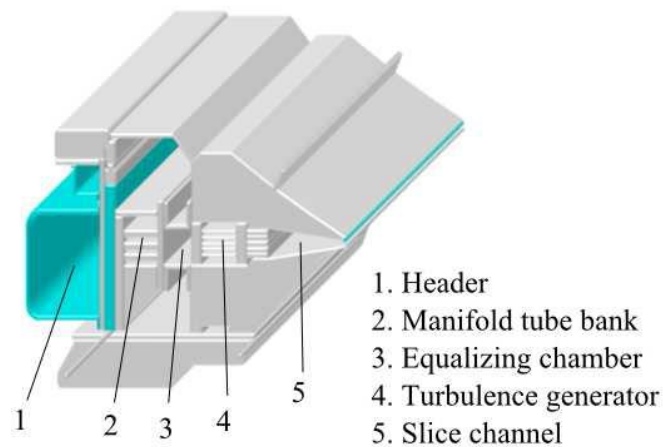


Figure 2.1. The structure of a modern headbox. Courtesy of Metso Paper, Inc.

The pulp slurry is initially fed to a header from which it passes into a manifold tube bank which spreads it across the entire width of the paper machine. Dilution water can be added to the pulp slurry in the manifold to control the basis weight of the sheet in the cross machine direction (Paulapuro 2000). The manifold

then feeds the pulp slurry to an equalizing chamber from which it continues to another set of pipes called a turbulence generator and subsequently to a slice channel. The slice channel terminates at a slice opening from which the pulp slurry is delivered to the forming section. Elastic plates (i.e. vanes) can be used in the slice channel to reduce large scale fluctuations in sheet structure and to maintain turbulence to improve sheet formation (Paulapuro 2000). Older machines, or machines which produce special paper grades, may have variants to the headbox structure presented in Figure 2.1.

The major task of the headbox is to produce the right type of jet for the forming section. Jet quality is determined by an even mass distribution in the cross machine direction; sufficient turbulence generation for the breakup of small fiber aggregates (flocs), and production of stable jets by pressure regulation. Jets leaving the slice opening have fiber a concentration that is governed by the paper grade, and is typically in the range of between 0.5 to 1.0wt% (Smook 2002).

From the headbox the pulp slurry is sprayed onto the forming section of the machine, which consists of a continuously moving fabric known as a forming fabric (or wire). Dewatering of the pulp slurry is the main task of the forming fabric. A secondary task of the forming fabric is to transport the developed sheet of fibers along the forming section of the process. In modern gap formers the forming section consists of two forming fabrics overlaying each other, the fiber pulp slurry is sprayed between them. The traditional Fourdrinier former consists of a single fabric onto which the pulp slurry is sprayed. Consequently in a Fourdrinier former dewatering occurs only in one direction through the forming fabric (Paulapuro

2000) as opposed to in two directions for a gap former. The majority of the free water removal that occurs in the making of a sheet of paper transpires within the forming section. When the pulp slurry leaves the forming section it has a solids concentration of 15 to 25 wt% depending on the paper grade (Smook 2002).

Dewatering can be enhanced by applying a vacuum on the opposite side of the forming fabric. Vacuum can be generated inside the forming roll, by the use of separate suction boxes, or zones. However, the most common means of amplifying vacuum is to employ blades in contact with the forming fabric. The dewatering components will be discussed in greater detail in Section 2.3. The forming phenomenon has a major influence on how evenly the fibers are distributed within the finished paper sheet. In the forming section, the accumulated fibers form an initial sheet which is called the wet web. Relative fiber position and orientation do not change extensively from the wet web structure to that of the finished sheet and thus sheet formation depends greatly on initial dewatering. Since formation is a significant measure of paper quality; it is obvious that control and manipulation of the forming section is critical to the papermaking process. Additionally, the greater the extent of water removal in the formation process, the less water need be removed in the more energy intensive processes of pressing and drying.

2.3. Components of the Forming Section

2.3.1. Forming Fabrics

Forming fabrics are a planar, continuous plastic woven mesh (Paulapuro 2000) that act both as a smooth support base for the fiber pulp slurry, and as a

filtration medium. The fibers that deposit upon or in between the forming fabrics create the wet web. Thus, the forming fabrics have a major effect on the finished product.

Commonly used fabric structures are so called single-layer (SL), double-layer (DL), triple-layer (TL), triple-weft (TW) and self support binding (SSB) structures (Smook 2002). These names refer to the number of fabric filament layers and their configuration within the woven fabric. Single-layer forming fabrics consist of only one layer of filament in each of two directions. Figure 2.2 presents an image of both sides of a single-layer forming fabric. The paper side is the side in contact with the pulp slurry, while the wear side is the side in contact with the machine.

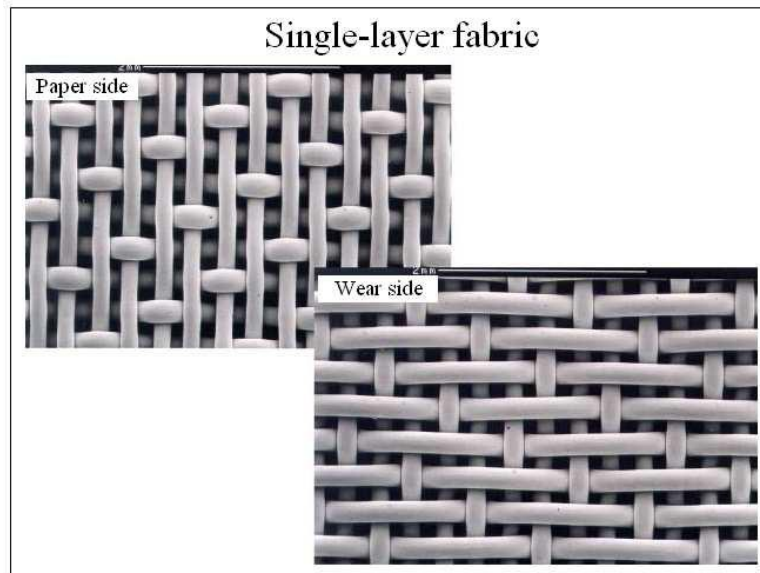


Figure 2.2. Single-layer forming fabric. © KnowPap.

Cross-section views of DL, TL and SSB structures are presented in Figure 2.3. The various weaving methods impart different structural properties and unique dewatering characteristics upon the fabric. The forming fabric has two important purposes: dewatering, and fiber-particle retention. Fiber retention is the ratio of

how much of solid pulp mass is retained for forming of the wet web, and how much is lost with the water during dewatering (Paulapuro 2000). Upon commencement of dewatering, a layer of fibers is quickly formed on, or between, the fabrics. This layer acts as a filtration base for later dewatering and wet web formation. Dewatering characteristics depend greatly on the forming fabric structure, specifically the pore size and tortuosity which are created by the various fabric weaves presented in Figure 2.3.

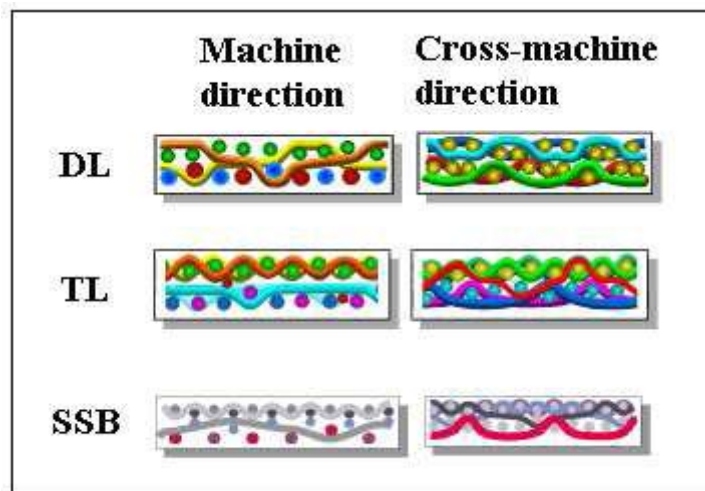


Figure 2.3. Examples of forming fabric cross-sections. Including double layer (DL), triple layer (TL), and support sheet binder (SSB). © KnowPap.

With a large pore size and low tortuosity dewatering is fast, however retention is poor as many fibers are not captured and are lost with the removed water. Conversely, a small pore size and a high tortuosity leads to a high degree of retention, but dewatering is slower [Paulapuro 2000]. As such, a compromise must be made between these two parameters.

2.3.2. Former Types

2.3.2.1. Fourdrinier Former

The Fourdrinier machine is the oldest former type in the papermaking industry. In this type of former the jet from the slice opening is sprayed on top of the forming fabric which moves in the horizontal direction. Figure 2.4 presents an example of a classic Fourdrinier former.

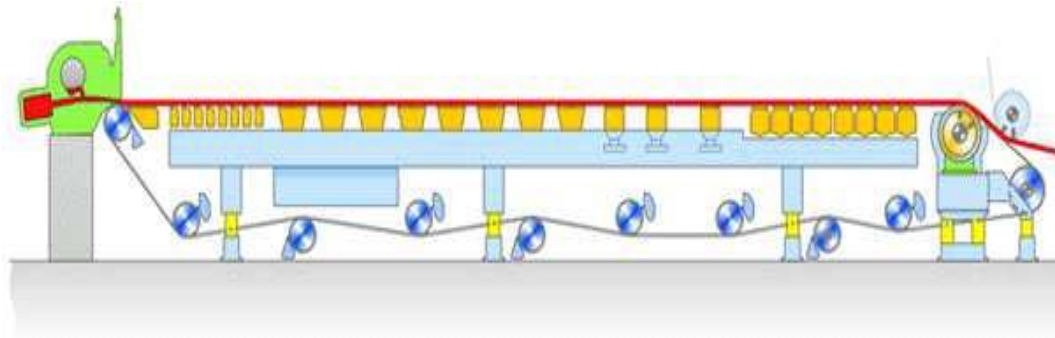


Figure 2.4. An example of a Fourdrinier former. From the headbox (green) the pulp slurry (red) is sprayed on the forming fabric. © KnowPap.

The image depicts a headbox on the left and a continuous forming fabric that revolves in the clockwise direction. At the end of the forming section the wet web leaves the former and is transported to the press section. In this type of sheet forming, dewatering occurs only in the downward direction through the forming fabric. Despite being the oldest type of former (introduced in ~1820), the Fourdrinier is still widely employed today. Originally gravity was the only force promoting dewatering in the forming section. Later developments introduced other dewatering elements such as foils, and both dry and wet suction boxes (Paulapuro 2000), which can be seen as yellow "boxes" in Figure 2.4. In addition, top (or Dandy) rolls may be used to press the wet web to squeeze water out through the

fabric. Fourdrinier formers have the advantage of gentle dewatering and a long dewatering time, which are required for some special paper grades. The major issue with Fourdrinier formers is that the one-sided dewatering leads to the web becoming “two sided” that is, having differing sheet characteristics on the two sides.

2.3.2.2. Twin-wire formers

The ever present tendency toward higher productivity goals leads to a constant drive for higher machine speeds. The Fourdrinier former configuration, however, produces unstable dewatering at higher running speeds. The industry solution to the problem was to introduce a second forming fabric, such that one is present on both sides of the wet web to stabilize the dewatering (Paulapuro 2000). In addition to improved stability, dewatering times became shorter since water was removed in two directions. The first twin-wire formers were developed in the early 1950s. Today these formers can be divided in two types: hybrid formers, and gap formers. As the name indicates, hybrid formers use both traditional Fourdrinier forming and twin-wire forming. An example of this kind of former may be seen in Figure 2.5. Apart from the upper forming fabric, the structure of this hybrid former is quite similar to the Fourdrinier former presented in Figure 2.4.

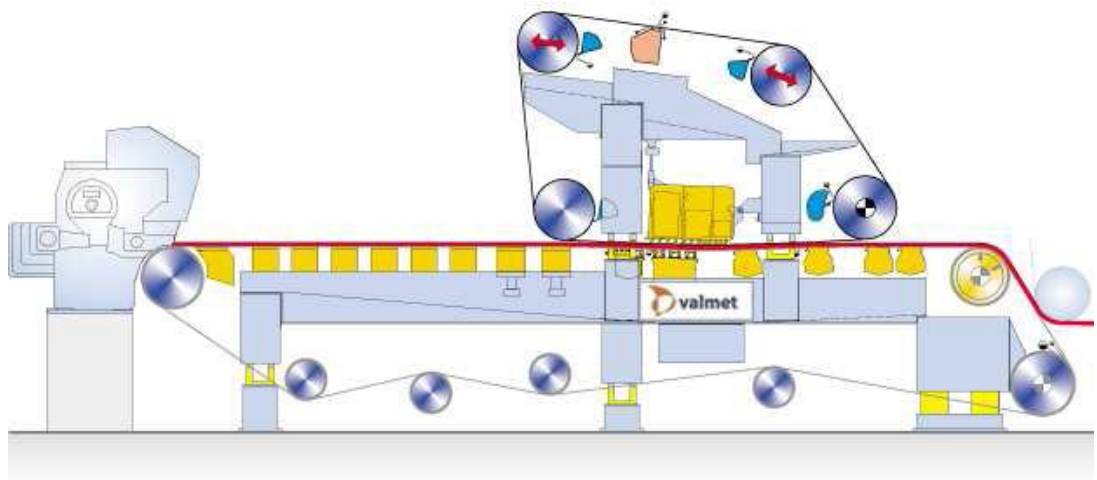


Figure 2.5. An example of a hybrid former. © KnowPap.

In gap formers the jet is sprayed directly between two forming fabrics and dewatering occurs through both fabrics. Thus, the forming section length may be greatly reduced in comparison with Fourdrinier or hybrid formers. Additionally, due to the rapid dewatering, forming fabrics need not be horizontal; as such the headbox angle can vary substantially. Figure 2.6 depicts an example of a gap former. The headbox is located at the bottom center of the image and is followed by two rolls carrying the forming fabrics which create the gap for the jet.

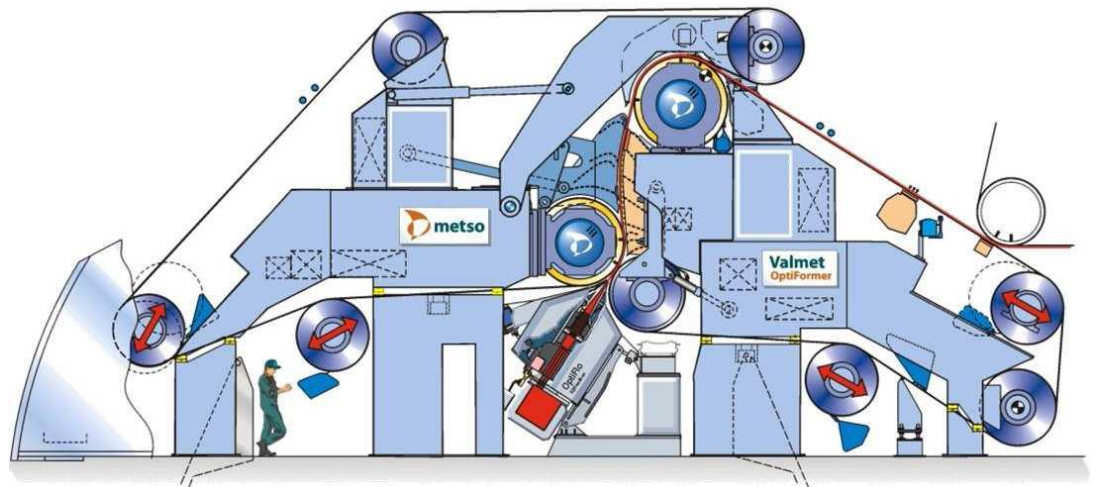


Figure 2.6. An example of a gap former. Courtesy of Metso Paper, Inc.

In gap formers dewatering is mainly derived by dewatering elements and by fabric tension, rather than by gravity. In a similar manner to hybrid formers there are dewatering elements on both sides of the wet web. Additionally, dewatering may be increased by creating a vacuum inside the forming roll. Dewatering in a modern gap former commences immediately after the headbox slice opening and is depicted in Figure 2.7.

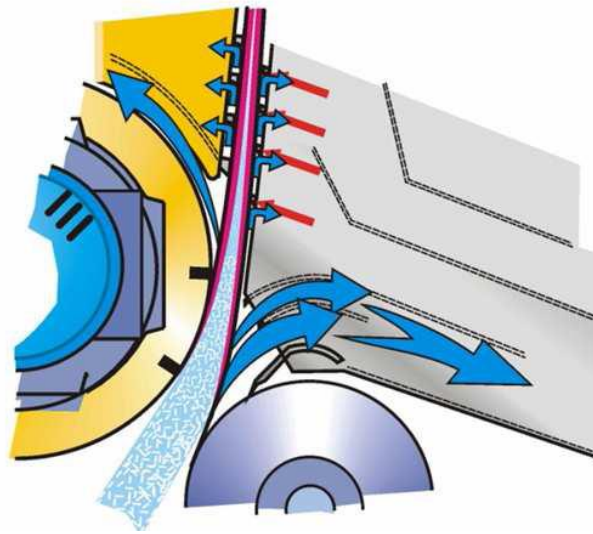


Figure 2.7. Jet from the headbox between the two forming fabrics of a gap former and initial dewatering. Courtesy of Metso Paper, Inc.

The use of twin-wire formers, such as a gap former, provides several advantages over Fourdrinier formers; increased dewatering capacity, more symmetric top and bottom sides of the resulting paper, lower basis weight variability, better formation, and lower linting (Paulapuro 2000).

A very significant parameter in the forming section is the jet-to-wire ratio. This parameter is defined as the ratio of the speed of the fiber slurry jet, to the speed of the forming fabric. The jet-to-wire speed ratio has a major effect on sheet

formation, for example it controls the fiber orientation anisotropy. The preferred jet-to-wire ratio depends on the paper grade produced, and the forming fabric type. Typically the jet-to-wire ratio has a value close to 1, but is varied to optimize sheet properties. (Smook 2002)

2.4. Drainage Theory

The primary process occurring in the forming section of a paper machine is drainage. The fundamentals of papermaking drainage may be examined from a theoretical perspective. During drainage, controlled filtration of a fiber slurry leads to the formation of a sheet. Filtration typically commences at a consistency in the range of 0.5 to 1.0 wt% fiber. As the papermaking process has evolved over the past century, researchers have continually attempted to model the process, and the rate of drainage, in order to enhance product quality, as well as to increase production rates. Today the most commonly accepted expression to describe the flow through the newly formed sheet in a Fourdrinier machine utilizes the Kozeny-Carman form of Darcy's Law:

$$\frac{\Delta P}{L} = \frac{\mu k (1-\varepsilon)^2 S^2 v}{\varepsilon^3} \quad (\text{Equation 2.1})$$

Where ΔP is the pressure drop across the thickness of the sheet, L is the sheet thickness, μ is the viscosity of the fluid, ε is the porosity of the bed, k is the resistance coefficient, v is the superficial velocity, and S is the specific surface area. This model predicts that as a sheet becomes thicker it requires a larger pressure gradient to produce the equivalent level of dewatering, similarly a thinner sheet

requires a lower pressure gradient. The porosity of the sheet also has a dramatic effect on the required pressure difference as it is inversely proportional and is a linear factor. A small increase in the porosity leads to a large decrease in the required pressure gradient for water removal.

2.5. Fundamentals of Pressing

Pressing operations represent the final opportunity to maximize the dryness of the sheet before entering the energy intensive dryer section. Pressing occurs in two regimes as described by Wahlstrom (1969); pressure controlled, and flow controlled pressing. In pressure controlled pressing the resistance to flow between the fibers of the sheet is insignificant. The dryness of the sheet is dictated solely by the flow of water exiting the fiber wall. Operation in the pressure controlled regime is preferred in industrial settings. Ceckler (1982) described pressure controlled pressing as a flow phenomenon with the press impulse being the major driving force. The amount of water that is removed is proportional to the basis weight of the sheet at the maximum operational pressure. A greater dryness can be achieved by increasing the pressure applied to the sheet, however, above the maximum operational pressure the structural integrity of the sheet is overcome and the sheet is crushed, creating a lower quality product. Pressure controlled pressing applies to single felted presses with basis weights up to 100 g/m² and to double felted presses with basis weights up to 150 g/m² (Wahlstrom 2001). The pressure controlled region can be extended to heavier sheets at higher speeds with modern shoe presses.

Conversely, flow controlled pressing is defined by conditions where the rate of water removal is constant at a given set of pressing parameters. This is a sign of poor operational pressing conditions (Smook 2002). In the flow controlled pressing regime water removal follows Darcy's law, as dryness is a function of the press impulse with no independent effect of pressure or time (Ceckler 1982). This condition arises when the water that is being pressed from the sheet is removed at a slower rate than it is created, defeating the purpose of applying a greater pressure. To overcome the limitation, the rate at which water is carried away from the pressing zone must be increased in order achieve a greater dryness out of the press and to revert to the pressure controlled regime.

2.6. Pressing Theory

2.6.1. Wahlstrom's Theory and the Four Phases of Pressing

The current understanding of pressing phenomena stems from the work of Wahlstrom (1960, 1969). Wahlstrom defines the pressing phenomena in papermaking as being comprised of two components for the flow of water; the flow of water between fibers, and the flow of water from fiber walls. Others have established sections of water removal in the press; however Wahlstrom (1969) has become the accepted standard for modern pressing theory. There are four identifiable phases of water removal in the press nip which Wahlstrom defines as shown in Figure 2.8.

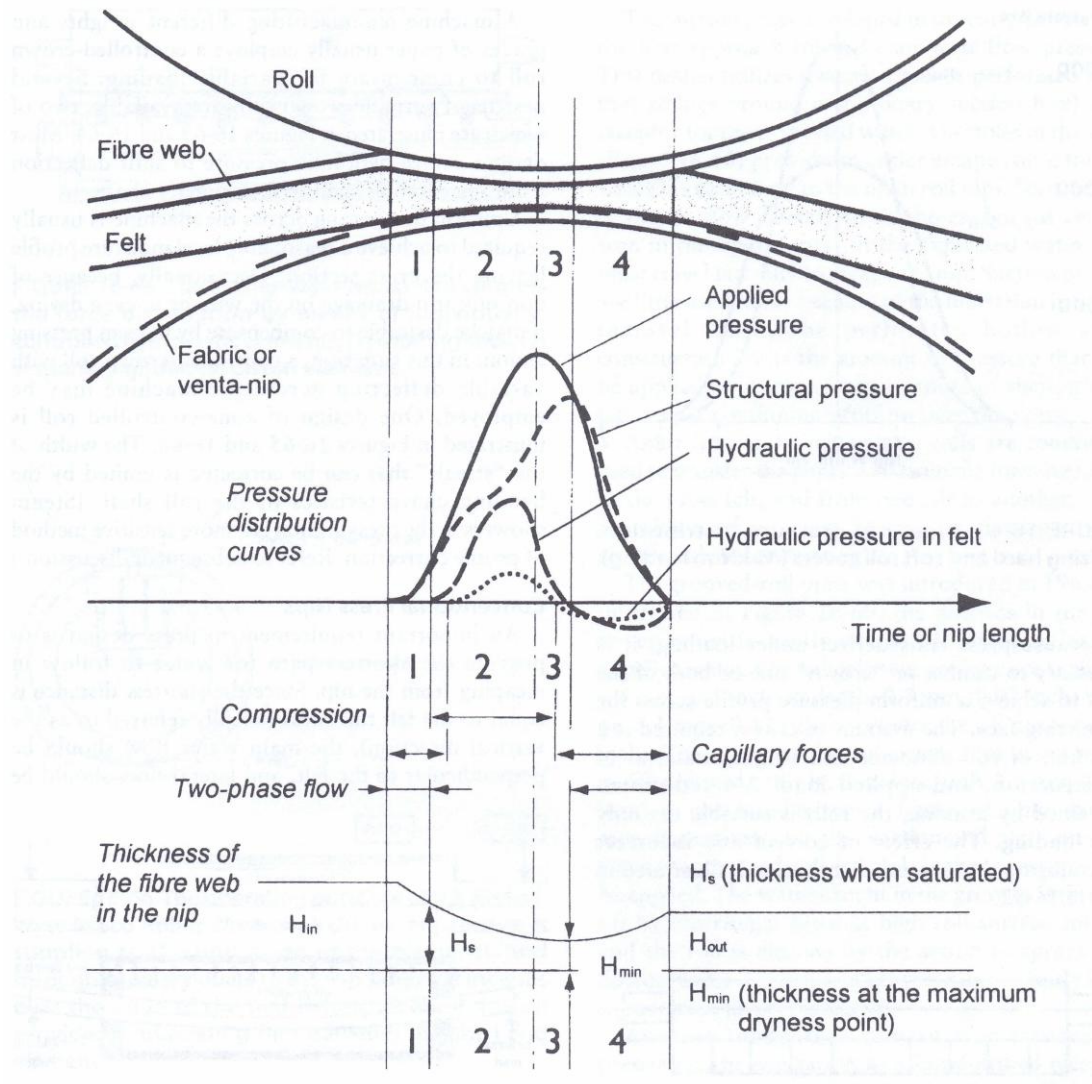


Figure 2.8. The four phases within the press nip as defined by Wahlstrom. (Smook 2002)

The first phase begins at the entrance of the press nip where the pressure curve commences, and ends when the paper has become saturated. In this phase the sheet and the press felt are compressed; removing air from both, however no hydraulic pressure is generated for water removal which leads to no change in the dryness of the sheet. This is due to the fact that the transfer of water out of the sheet can only occur through capillary forces or evaporation. The second phase continues from the point of saturation to the mid-nip point where the maximum

total nip pressure is applied. The now saturated sheet is exposed to increasing mechanical pressure, generating a hydraulic pressure within the sheet which drives water from the sheet into the press felts. During this phase the press felts also reach saturation and water may begin to flow out of the felt into receptacles in the press roll. Press rolls, which provide pathways for water to enter, are either vented rolls or are suction rolls. The hydraulic pressure in the paper reaches a maximum before the mid-nip point. It is noted that there are capillary forces which induce water transfer from the sheet to the felt prior to the felt becoming saturated. In phase three, pressure is maintained until the pressure gradient within the sheet becomes zero, indicating the maximum dryness achievable in the press. As the nip opens, the paper remains compressed while the felt begins to expand. As the felt expands it becomes unsaturated which creates a vacuum, pulling air and water into the felt. The fluid flow of water is ongoing and capillary forces assist in the transfer of water from the sheet to the felt. The sheet reaches its maximum dryness as it enters phase four of the press nip. As the pressure is released the sheet and felt expand, creating a negative pressure gradient which allows water to return to the unsaturated sheet. Capillary pressure also acts to reabsorb water into the sheet from the felt. The phenomenon of water returning to the sheet is known as rewetting and will be discussed in Section 2.6.3.1.

2.6.2. Capillary Forces in Paper

The major resistance to water transfer out of the sheet in pressure controlled pressing is the large capillary pressure experience by the unbound water within the

fiber walls (Wahlstrom 1960). In addition, the sheet itself introduces another mechanism of trapping unbound water within the newly formed voids between fibers which were nonexistent prior to individual fibers forming the sheet. With the knowledge that the fiber wall can retain 1 to 4 kg of water per kg of fiber exiting the press section (Wahlstrom 1981), it is clear that an understanding of the factors that govern water removal from capillaries (and voids modeled as capillaries) is critical in order to maximize the dryness achievable exiting a press.

The Young-Laplace equation describes the equilibrium pressure across the interface of two static fluids (air and water). Solving the Young-Laplace equation for capillary pressure in a cylinder, results in determination of the force required to initiate water movement in capillaries within the fiber wall and within the sheet.

$$\Delta P = \frac{2 \cdot \gamma_{lg} \cdot \cos(\theta_{ls})}{r} \quad (\text{Equation 2.2})$$

Where ΔP is the pressure difference across the liquid-gas (water-air) interface, γ_{lg} is the liquid-gas (water-air) surface tension, θ_{ls} is the solid-liquid (fiber-water) contact angle, and r is the capillary radius. The difference in pressure represents the total force which holds the water trapped within a capillary and which must be exceeded in order to remove the water. By manipulating the surface tension, contact angle, or the pore radius of the capillaries within the fiber wall or sheet, the total pressure needed to initiate water removal can potentially be decreased. This methodology would allow for the constant pressure applied in the

pressure controlled pressing regime to be more efficient at removing unbound water, leaving only the remaining bound water to be removed by other means.

Darcy's law can be used to describe the flow of water out of a sheet from between fibers, and from within fiber walls (Wahlstrom 1960). Darcy's law is a proportional relationship between the flow rate through a porous medium, in this case the sheet or fiber wall, the viscosity of the fluid, and the pressure drop over a given length.

$$Q = \frac{-\kappa \cdot 2\pi r^2}{\mu} \cdot \frac{(P_b - P_a)}{L} \quad (\text{Equation 2.3})$$

The flow rate, Q , is equal to the product of the permeability, κ of the medium, the cross-sectional area of the flow, and the pressure drop ($P_b - P_a$), all divided by the dynamic viscosity, μ and the length, L over which the pressure drop is occurring. The negative sign arises from the fact that the fluid flows from regions of high pressure to low pressure. If the pressure drop is defined such that P_a is the capillary pressure holding water between fibers or within the fiber wall and P_b is the applied hydraulic pressure created in the press nip, Darcy's law can be used to describe the flow of water out of the sheet and into the press felts.

2.6.3. Pressing Variables in Water Removal

Several authors have compiled lists of variables which control, or have major influences on, water removal from a sheet during pressing. Building on work performed by Robertson (1976), Bliesner (1978), and Wahlstrom (1969), Busker (1984) defined primary and secondary wet press variables. Primary variables are

those which influence the dryness of the sheet leaving the press section by greater than 2%, while secondary variables are those that have effects of 2% or less on the dryness exiting the press section. The present review focuses on the primary variables where the largest gains can potentially be made.

2.6.3.1. Post Nip Rewet

A major variable mentioned in Section 2.6.1 previously is post-nip rewet of the sheet. Post-nip rewet occurs during extended contact between the felt and the sheet after the maximum nip pressure point. Even with the rate of water transfer being very low in this scenario, Busker (1984) states that post-nip rewet can account for up to 5% of dryness loss exiting the press nip. Thorne (1981) previously demonstrated decreasing dryness through rewet by measuring 7 to 37 g/m² of water uptake in a 300 Canadian standard freeness (CSF) sheet at contact times of 39 ms to 628 ms. Light weight sheets are more susceptible to rewet due the high ratio of sheet surface area to basis weight, which allows for a greater fraction of the total capillaries within the sheet to be exposed to the excess water within the felt. Comparatively heavy weight sheets such as linerboard can lose as little as 2% dryness due to rewet (Busker 1984).

2.6.3.2. Ingoing Sheet Dryness

The ingoing sheet dryness is known to have a large effect on the outgoing sheet dryness as reported by Smart (1975). At the typical 35 to 40% sheet dryness level out of the press, a near linear relationship is observed where an approximately

2% dryer sheet entering the press leads to a 1% dryer sheet exiting the press. From this general relationship, ratios in the range of 2:1 to 3:1 dryness in to dryness out are used to approximate gains in industry (Busker 1980). The in-going sheet dryness determines the water load at the nip and is usually an uncontrolled variable. However, sheet basis weight can control the amount of water carried through the presses, where heavier sheets retain more water. Busker (1980) showed that a change in basis weight from 60 to 163 g/m² corresponded to a change in sheet dryness from 44% to 37% at constant pressing.

2.6.3.3. Sheet Temperature

During pressing the sheet temperature has a significant effect on water removal. The addition of steam boxes and other heating elements, such as infrared heat sources, to press sections have contributed to recent improvements in pressing operations (Smook 2002). By raising the temperature of the sheet and the associated water, the viscosity of water within the sheet decreases allowing for easier removal in the press section as predicted by Darcy's Law (Equation 2.3). Wahlstrom (1991) states that for each 10°C increase in sheet temperature, a 1% increase in sheet dryness results experimentally, which is comparable to predictions by Darcy's Law (Equation 2.3). Anderson and Back (1981) demonstrated a change in dryness out of the press from 38% to 48% for a sheet temperature change of 5°C to 90°C. However, due to the high partial pressure of steam at 80 to 85°C, it is uneconomical to further increase heating in the press section. Similarly, Busker (1984) presented an increase in dryness out of the press of 0.6 to 1.1% for every

11°C rise in sheet temperature by applying steam to the sheet prior to the nip point. The application of steam to the sheet is currently achieved by placing steam boxes at the entrance of the nip. Recently, the introduction of the heated press roll, which aids in flashing off some water and also lowering water viscosity, has resulted in improved water removal (Smook 2002).

2.6.3.4. Furnish Properties

The furnish properties of the slurry employed to form a sheet provide another major variable in pressing. The amount of refining of the stock provides a controllable parameter of sheet dryness; whereby a sheet with higher refining shows a higher wetness as described by Busker (1984). A bleached kraft sheet demonstrated an increase of 15% wetness when refined from a Canadian Standard Freeness of 720 to 200. The pulp type also affects water retention as kraft fibers retain less water than ground wood fibers (Caulfield 1982).

Recalling that the capillary forces present in-between fibers and within fiber walls dictate the pressure required to remove water during pressing, manipulating the surface tension, contact angle, or the pore radius of the fibers or sheet with additives in the furnish may provide an increase in dryness out of the press; however, literature is lacking in this area. To further demonstrate that the industry has possibly ignored this aspect of pressing, Busker (1984) states that “[additives] are not apt to be the most productive areas of research and development for large gains.”

2.6.3.5. Press Loading and Nip Residence Time

A major parameter in pressing is the extent of press loading and nip residence time. The pressure controlled regime is of course limited by the structural integrity of the sheet (Caulfield 1986). Campbell (1947) was the first to suggest dryness is proportional to the product of pressure per unit area and the time of application (the press impulse). This was later studied by Wahlstrom (1969) and examined in detail by Ceckler (1982). The press impulse is the through sheet component of the applied force integrated over the time that the sheet spends in the nip zone. The greater the impulse in the press nip the higher the generated sheet dryness. As demonstrated by Busker (1984) a 1 psi-s impulse on a light weight sheet produces a dryness of 30%, while a 100 psi-s impulse produces 60% dryness. Building on the concept of press impulse, Beloit developed the shoe press. The shoe press increases the total time the sheet is exposed to the nip by creating a wider nip point (Smook 2002). The image presented in Figure 2.9 is a current shoe press design by the Andritz Group.

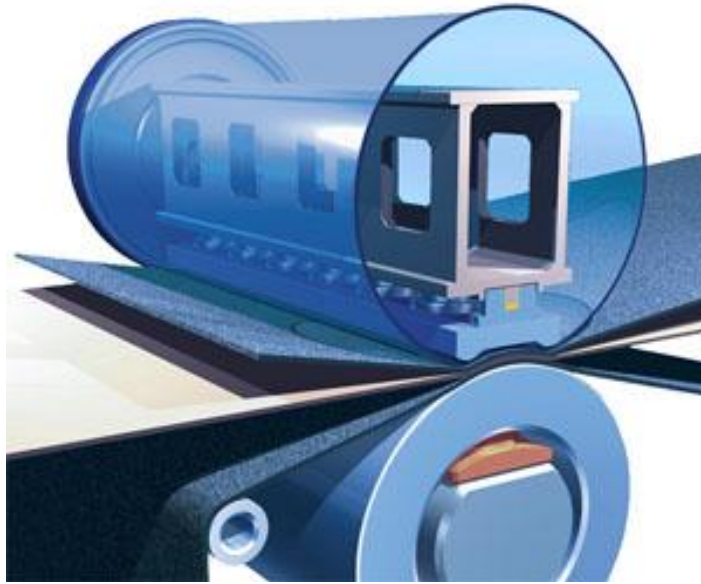


Figure 2.9. Modern shoe press, the X-Nip by Andritz. Courtesy of Andritz

The shoe press makes use of a concave shoe pressing against a rubber belt to apply pressure to the sheet against a lower press roll. The wider the shoe the wider the nip point is in the press. This allows for a greater total press impulse and increased sheet dryness. Wahlstrom (1991) estimates that a shoe press can increase sheet dryness by 4 to 5 wt%, corresponding to 20% production increases in linerboard and corrugated media.

2.7. Pressing Advancements

Methods of enhancing the rate of water removal from the press have largely centered on mechanical construction. Press felt suppliers have continuously developed press fabrics which withstand greater nip pressures, while providing greater permeability at the nip and subsequently yielding greater water removal. Separately, press roll development has resulted in the creation of further pathways for water removal. In additions, press section designers have gradually developed

press sections with a greater number of nip points and larger residence times within the nips. Recent research has also been conducted in impulse drying to further enhance water removal.

2.7.1. Press Felts and Rolls

New designs for press felts and press rolls have made great strides in enhancing the efficiency of water removal in the press section. The ideal press felt is one that can resist high compression resulting from high press impulses, and be able to handle large water capacities. Ideally this would be done while providing a low resistance to flow into the press felt and a uniform pressure across the web. Varying weave patterns and construction materials have been employed to meet the minimum of these needs to date; however, suppliers are continually attempting to design better press fabrics. Synthetic felt construction materials have taken over where wire meshes and cotton felts once were the norm (Wahlstrom 2001).

Historically the development of the press roll has concentrated on optimizing the surface (specifically to provide better release of the wet sheet). Traditionally, press rolls were polished granite, however, due to failures of granite rolls at high speeds and the inability of granite to take the temperature shock which comes with the addition of steam boxes, modern press sections are commonly equipped with composite type rolls (Smook 2002). The new generation rolls have a steel core with a composite cover to mimic the properties of granite rolls. Using grooved and drilled rolls gives the water other means of exit from the nip. Suction rolls have also

recently come into use and are currently employed on lightweight and fine paper grades. (Smook 2002)

2.7.2. Press Configurations

Press configurations have undergone many modifications to provide more compact press sections, and generate optimal water removal. Initial press section designs were a straight-through configuration (Smook 2002). This design carries the sheet from one set of press rolls to the next with a press felt on the wire side of the sheet and a hard roll on the top side as shown in Figure 2.10.

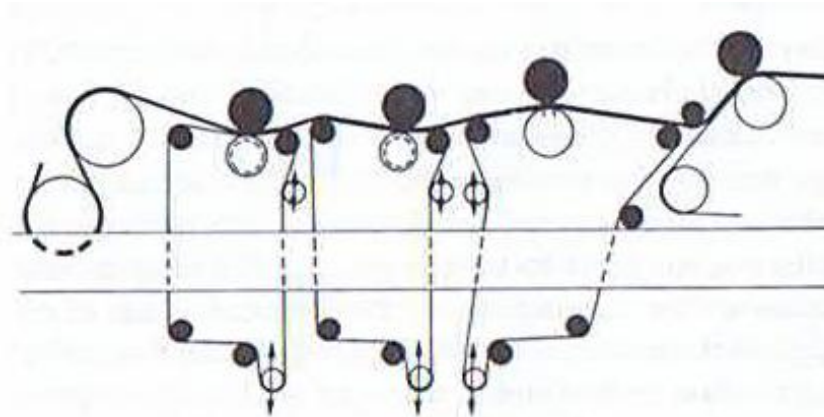


Figure 2.10. Straight through press section. (Smook 2002)

Later improvements to this design included a suction roll to pick up the sheet from the forming section, and the addition of a top felt, thereby beginning the trend of double felting press sections. The top or second felt allows for the sheet to be pressed in between two similar surfaces, thus reducing the two sidedness of the sheet. The next step in development of press configurations was the transfer press, which utilized a suction roll to allow for the pick-up of heavier and wetter sheets from the couch roll. Several configurations have provided recent advancements in

pressing, such as the twinver press. The twinver press was one of the first press section designs to incorporate a no-draw press. The no-draw press, which eliminates the gap between the couch roll and the press pick-up roll, provides support for lightweight sheets at high speeds and therefore allows for an increase in production (Smook 2002). Further developments have led to three-nip no-draw press sections with double felted nips as shown in Figure 2.11. The three-nip no-draw press section uses four rolls in contact to create three nip points where the sheet is pressed on both sides, reducing both two sidedness and water load.

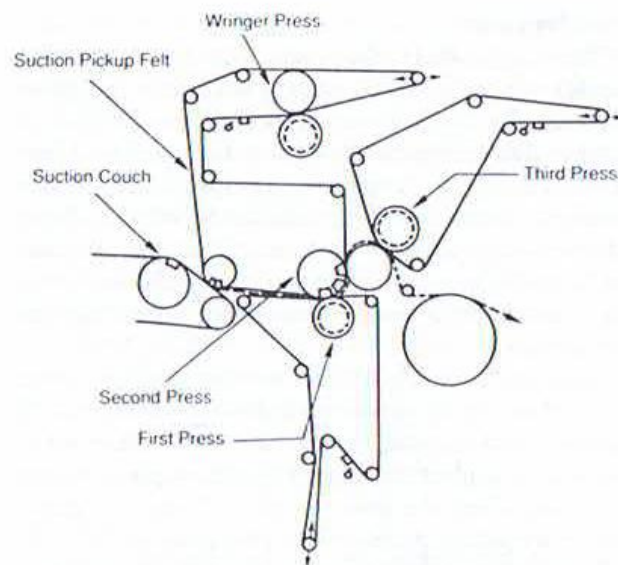


Figure 2.11. Three-nip no-draw press section arrangement. (Smook 2002)

2.7.3. Impulse Drying

At the forefront of mechanical pressing technology and development is impulse drying. Wahlstrom (2001) states "... [Impulse drying] is the only technology presently on the horizon that offers the potential of increasing press dryness to levels above 60%." Impulse drying or pressing, not to be confused with

the press impulse, is performed by pressing the sheet against a heated roll. The roll is heated to between 200°C and 400°C, which generates steam in the expanding section of the nip point. This steam forces water held within the sheet out (Wahlstrom 2001). For generation of steam, the press impulse must not be too short. Due to the large press impulse required, stemming from the extended residence time necessary to induce the generation of steam, this technology is currently applied largely to shoe press configurations. Work performed by Lucisano (2003) and furthered by Backstrom (2009) has shown that impulse technology can improve dewatering, mechanical properties of the sheet, and printability of the sheet. Backstrom (2009) determined that impulse pressing can possibly increase paper machine production by up to 40% if it is dryer section limited.

2.8. Chemical Enhancements to Pressing

Little work has been reported examining if and how pressing can be enhanced by means other than mechanical. Stratton (1982) utilized various cationic wet end polymers to demonstrate that increases of 1-2% solids of out of a press section were possible with varying dosage levels. The study focused solely on the use of polymers in wet pressing. Higher polymer doses resulted in larger solids increases. High charge density polymers were found to be more effective than low charge density polymers (Stratton 1982). At the time, Stratton stated that the mechanism for the effect had not been determined.

Wegner (1987) studied the effects of cationic polyacrylamide on water removal in the forming, pressing, and drying sections. Wegner observed that while

an increase in drainage was evident, the sheet behavior during wet-press dewatering was unaffected. It was noted, however, that wet pressing with a cationic polyacrylamide could compensate for higher moisture levels entering the press while maintaining the solids content exiting the press (Wegner 1987).

Work performed by Springer (1991) demonstrated that chemical additives had an indirect influence on wet pressing. Chemical additives affecting drainage prior to the press resulted in higher solids into the press section and ultimately higher solids exiting the press (Springer 1991). Additional research showed that for sheets entering the press at equal moistures, the additives had no effect on the outgoing solids content. Springer (1991) postulated that if an additive was to have any effect on press enhancement, the additive must be able to penetrate the fiber structure and influence its water holding capacity. Given the findings of Springer (1991), it is evident that a thorough understanding of cellulose fiber structure and the factors that may affect water holding capacity are required. Combining this understanding with the effect of a potential chemical additive may yield a mechanism for water removal, further discussion is provided in Section 2.11.

2.9. Surfactants and Adsorption

In examining the potential of chemical additives to enhance dewatering it is noted that the pulping process generates several types of bonding sites on the wood fiber that may potentially be used for surface modification. In addition to the native hydroxyl sites that cellulose exhibits, there are many carboxylic acid groups which form on the surface of the fibers during pulping. These groups can dissociate,

thereby forming sites for electrostatic interactions. These electrostatic sites may be targeted for surface modification, specifically by surfactants or charged polymers.

2.9.1. Surfactants

Surface active agents, or surfactants, are organic compounds that are amphiphilic, i.e. they contain both hydrophobic groups, known as tails, and hydrophilic groups, known as heads (Moore 1972). Due to their amphiphilic nature, they are typically soluble in both organic solvents and water. The type of head group is used to classify surfactants into four categories: anionic, cationic, non-ionic and zwitterionic (amphoteric) (Moore 1972). Their amphiphilic nature leads to a driving force for surfactants to migrate and adsorb, or self-assemble, at interfaces, e.g. liquid/gas, liquid/liquid and solid/liquid. At the liquid-gas interface (e.g. water/air), surfactants act to reduce the surface tension. Similarly, they can reduce the interfacial tension between two liquids by adsorbing at the liquid/liquid interface. Liquid/solid interfaces may also be modified by adsorption of surfactants, leading, for example, to changes in surface energy, and the contact angle of liquids on the modified surface. Above a threshold concentration, surfactants assemble in bulk solution forming aggregates known as micelles. The concentration at which surfactants form micelles is referred to as the critical micelle concentration (CMC). When micelles assemble in water, the hydrophobic tails of the surfactant create an inner core and the hydrophilic head groups form an outer shell that maintains favorable contact with water creating a minimum in the free energy (Moore 1972).

2.9.2. Surfactant Adsorption

Application of surfactants to modify the surface of cellulose fibers through the process of self-assembly has been examined by Aloulou (2004) and Alila et al. (2005, 2007). The adsorption of a surfactant on a cellulose surface is classified as self-assembly as shown by Alili et al. (2007). Electrostatic forces and the hydrophilic nature of the surfactant and cellulose fiber provide non-covalent contributions to the bonding. The alkyl chain of the surfactant contributes entropic driving forces for adsorption.

The surface of a wood fiber, comprised primarily of cellulose and carboxylic acid groups formed during pulping, provides an abundance of polar bonding sites. This allows for adsorption of various hydrophilic head groups. Work completed recently by Aloulou (2004) investigated the adsorption of a cationic surfactant onto cellulosic fibers. Alila et al. (2005) demonstrated that adsorbing a cationic surfactant onto a cellulose surface created an increase in the zeta potential of the cellulose as shown in Figure 2.12 (Alila 2005).

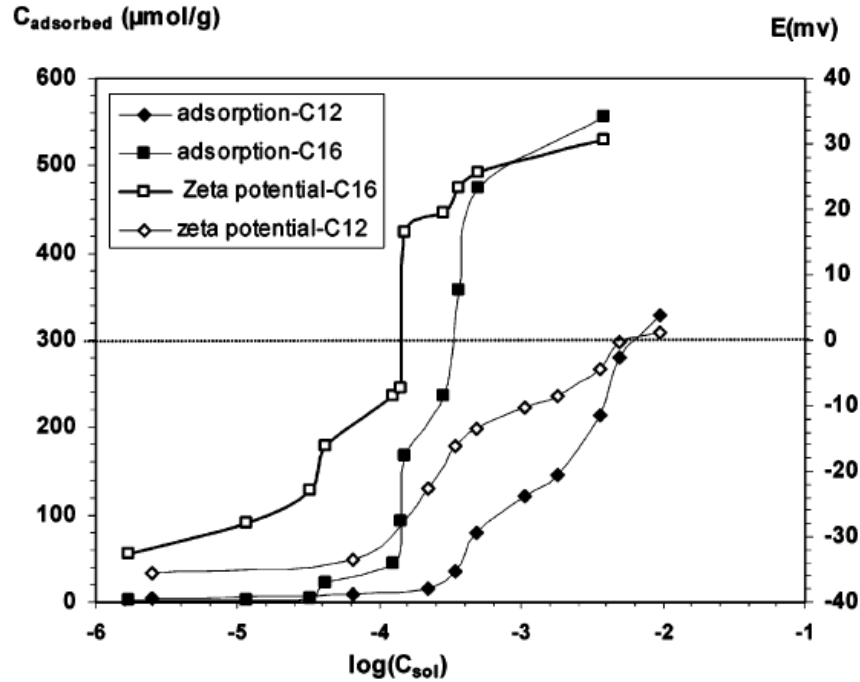


Figure 2.12. Adsorption of cationic surfactants on cellulose fibers. Zeta potential versus solution concentration (Alila 2005).

The zeta potential is the electric potential of the interfacial double layer at the slipping plane, versus a point in the bulk fluid away from the colloidal interface (Moore 1979). That is, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the surface. The dispersion medium in a pulp slurry is the water surrounding the cellulose fibers and the stationary layer of fluid is considered to be the bound water on the fiber. The change in surface energy of the cellulose fiber likely leads to changes in the behavior of cellulose surface interactions (e.g. fiber-fiber, fiber-water, etc.).

In addition, Alila et al. (2005) measured adsorption isotherms of cationic surfactants with varying alkyl chain lengths on cellulose surfaces to determine the dependence of adsorption on the chain length. Surfactant alkyl chain lengths of C₁₂, C₁₄, C₁₆, and C₁₈ were employed for adsorption onto model cellulose surfaces. Figure

2.13 reprinted from Alila et al. (2005) demonstrates that increasing surfactant chain length leads to a shift of adsorption toward lower concentrations and to a continuous increase in the maximum adsorbed amount of surfactant (Alila 2005). This trend is attributed to the entropic driving force derived from the hydrophobic surfactant tails.

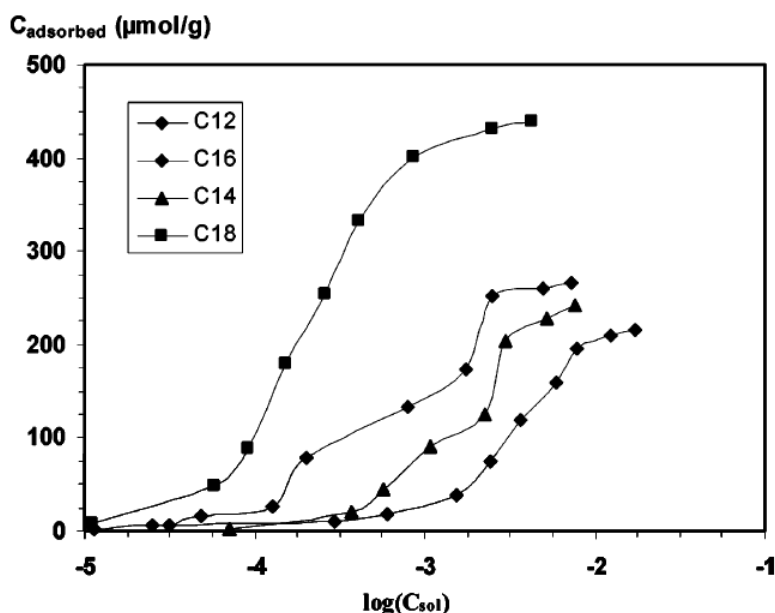


Figure 2.13. Adsorption isotherm of C₁₂, C₁₄, C₁₆, and C₁₈ cationic surfactants onto cellulose. (Alila 2005)

2.10. Pulp Modification

Chemical modification of pulps to enhance pulp strength, color, and water holding capacity, specifically for recycled pulps, has been a topic of much research (Wistara 1999, Smook 2002) due to the present trend of reusing and recycling paper. It is well known that the strength, color, and water holding capacity of recycled pulp are far inferior to virgin pulps and any improvement in the performance of those pulps would allow the use of a low cost raw material. A study

by Wistara and Young demonstrated that while some properties of a recycled pulp can be improved by chemical treatments, other aspects of the pulp are negatively affected (Wistara 1999). Specifically, the relationship between the ability of the pulp to hold water, and the tensile strength of the paper was examined. Wistara and Young treated recycled pulp with butylamine and ammonia and found that the treated pulps had lower hydroxyl contents. The water holding capacity decreased after the treatment; however paper made from the pulps demonstrated a decrease in tensile strength. Wistara and Young hypothesized that the reduction in the number of hydrogen bonding sites (hydroxyl groups) was responsible for the decrease in fiber-fiber bonding strength, as evidenced by the lower tensile, and for the decrease in water holding capacity due to a reduction in hydrophilicity of the fiber surfaces (Wistara 1999).

2.11. Present Opportunity

Decreasing the water load entering the drying section of a paper machine, and/or decreasing the energy required to evaporate the residual water, is expected to result in significant energy, and hence fiscal savings. The vast majority of efforts made to increase the amount of water removed in the forming and pressing operations to date have focused on mechanical methods. Specifically, most work has centered on new forming section designs, wire construction, means of extending pressure impulse, improving felt and roll design, and introducing new press section configurations. An alternative and little explored methodology is to reduce the hydraulic force required to overcome the capillary force holding water within the

fiber walls and between fibers through the reduction of the capillary force itself. Additionally, the concept of modifying the energetics of water bonding to cellulose to reduce the thermal energy required to evaporate bound water has not been pursued. The fundamental parameters that govern water removal from capillaries within fiber walls and between fibers are known. Specifically, the relevant parameters are given by the Young-Laplace equation and are the water/air surface tension, the cellulose/water contact angle, and the pore radius. Surfactants are known to adsorb on cellulose (cationic surfactants in particular) and hence affect the surface energy and consequently the contact angle. Additionally, surfactants modify the water/air surface tension. Thus at least two of the relevant parameters may be positively modified through judicious application of surfactants. Consequently the present work investigates, from both a fundamental and an applied perspective, the effect of surfactant addition on the dewatering of paper in the forming and press sections, and the energetics of residual water removal in the dryer section.

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1. Materials

3.1.1. Fibers

In order to determine the effectiveness of a given water removal technology, experiments must be performed on a papermaking slurry and the subsequent sheet, the primary constituent of which is cellulose fibers. Cellulose fiber sources differ greatly around the world, and it is clearly impractical to attempt work with every know fiber. As such the present work took a targeted approach and worked with both virgin and recycled fibers that are dominant in the papermaking industry of the Northeastern United States.

3.1.1.1. Virgin Fibers

Virgin fibers are cellulose fibers that have not previously been formed into products such as paper or board. These unprocessed fibers are generally favored for their strength, color, and overall ease of manipulation since the fibers have not previously been damaged or fibrillated. The dominant source of virgin fiber employed in the present work was Sappi Fine Paper's Co-Pulp which is a 15% hardwood, 85% softwood kraft fiber blend. This fiber was obtained from the Process Development Center at the University of Maine. Several other virgin fibers were employed to a lesser extent in the present work. A sulphite softwood pulp was acquired from the Twin Rivers Paper Company. A 100% softwood kraft pulp was

acquired from Fibrek, as well as an unbleached kraft fiber pulp. These pulps were received in dry lap form and were rehydrated to 4 wt% consistency in a two liter TAPPI disintegrator for seven minutes prior to use to mimic the hydro pulping stage of the paper making wet end process.

3.1.1.2. Recycled Fibers

Recycled fibers are cellulose fibers that have been re-pulped or re-disintegrated from an existing cellulose containing product such as paper or board. Papermakers differentiate between fibers that are recycled from post consumer products; including but not limited to newspaper, corrugated cardboard, paper board, and coated paper; and fiber recycled onsite at the mill due to manufacturing issues. The later is referred to as broke fiber and is simply re-disintegrated prior to use. Post consumer fiber is initially processed at fiber recycling facilities to remove inks, glues, and additional contaminates, before being utilized in the papermaking process.

In the present work, recycled newsprint and directory fiber was supplied by Armstrong World Industries. The fiber was received in sheet form and required bench top disintegration prior to use; the pulps were not deinked or otherwise treated prior to testing. Recycled brown fiber (post consumer) was acquired from Fibrek, which had been fully processed and re-pulped.

Broke fiber was obtained from multiple sources. Single side coated broke was supplied by the Twin Rivers Paper Company to enable simulation of filler and fines in the papermaking process. Directory broke was acquired from the former

Kathadin Paper Company. Both of these pulps were rehydrated and disintegrated prior to use.

3.1.2. Water Removal Additives

A set of screening experiments was performed to measure the effect of an assortment of additives on fiber water retention in an attempt to identify which parameters of the Young-Laplace equation could be manipulated. As previously discussed, work completed by Aloulou (2004) and Alila et al. (2005) demonstrated that cationic surfactants adsorb at the cellulose/water interface. As such cationic surfactants were employed in the present work to modify the surface tension and potentially the cellulose/water contact angle. A model cationic surfactant, cetyltrimethylammonium bromide (Sigma, approximately 99%) ($[(C_{16}H_{33})N(CH_3)_3Br]$ (hereinafter CTAB) depicted in Figure 3.1, was selected due to its known adsorption on cellulose (Alila 2005), the extensive body of literature that exists on its colloidal and interfacial behavior, and its ready availability.

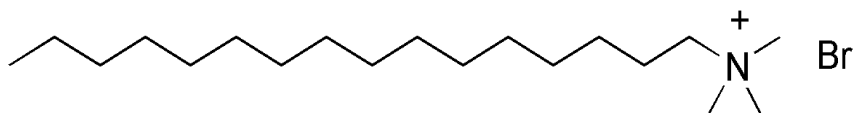


Figure 3.1. The chemical structure of cetyltrimethylammonium bromide (CTAB)

In order to differentiate the potential effect of surface tension and adsorption on dewatering, a range of surfactants with the same cationic head group but varying chain lengths were examined specifically, octadecyltrimethylammonium bromide (Sigma-Aldrich, approximately 99%) (hereinafter OTAB) ($[(C_{18}H_{37})N(CH_3)_3Br]$) was employed, as was a generic alkyltrimethylammonium bromide mixture (Sigma,

95%) (hereinafter Cetrimide), which was predominantly $((C_{14}H_{29})N(CH_3)_3Br)$ but also contained C_{12} and C_{16} homologs.

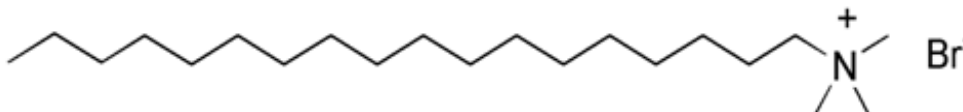


Figure 3.2. The chemical structure of octadecyltrimethylammonium bromide (OTAB).

In order to examine potential effects of surfactant head group charge on dewatering, two anionic surfactants sodium dodecyl sulfate (SDS) (Sigma-Aldrich 99+% ACS reagent) and lignosulfonic acid (Aldrich, sodium salt, desulfonated) were examined as was a non-ionic surfactant, Triton X-100 (Sigma-Aldrich).

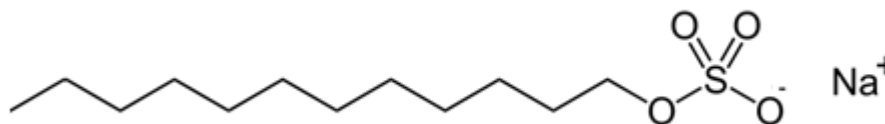


Figure 3.3. The chemical structure of sodium dodecyl sulfate (SDS).

In addition to screening the effectiveness of a range of surfactant species not previously examined in the literature, the opportunity was taken to examine additives previously reported to be effective. Firstly, an additive that anecdotal evidence had suggested is effective in altering the extent of the water retention of fibers was studied. Specifically, the effect of a cationic polymer widely used as a paper making retention aid, BASF Percol 182, was employed. Secondly, the effect of colloidal silica (Aerosil 380, silica powder) was studied due to a personal communication (Bilodeau 2007) stating that it is suspected by some in the industry of decreasing water retention values through lumen loading.

3.1.3. Paper Making Additives

In an effort to as closely as possible duplicate the wet end chemistries of the papermaking process, industrially employed wet end chemicals were sourced. Specifically, BASF's Telioform system was employed as it is the industrial standard in wet end systems. The Telioform system affects retention, drainage, and formation, thereby allowing a single system implementation to mimic a wide range of papermaking chemical additive functions.

The Telioform system is a dual microparticle system comprising two microparticles; BASF Telioform M306 (an anionic micropolymer) and BASF Hydrocol 2D6 (bentonite). The specific bentonite employed in the Telioform system is the sodium montmorillonite form of the smectite trioctahedral swelling clays. The bentonite has a plate-like structure that is positively charged on the edges and negatively charged on the flat surfaces. Also included in the Telioform system are BASF Percol E22S, a cationic microemulsion retention aid, and BASF Alcofix 189, a cationic low molecular weight polyamine retention aid.

3.2. Experimental Methods

3.2.1. Water Retention Value Testing

The water retention value (WRV) is a laboratory scale comparative measure of water content in a paper mat after the press section of a paper machine (TAPPI UM 256). The WRV is the most widely employed pulp quality measurement examined in wet pressing studies (Wahlstrom 2001). The WRV test is employed to simulate how much water remains after the pressing operation and hence how

much water must be removed by subsequent thermal treatment. The test requires a 40 g sample of pulp to be centrifuged at 900 G for 30 minutes and weighed. The sample is subsequently oven dried for a minimum of 12 hours and reweighed. The WRV is calculated via Equation 3.1:

$$\text{WRV} = \frac{\text{Weight of Pad After Centrifuging} - \text{Weight of Oven Dried Pad}}{\text{Weight of Oven Dried Pad}} \quad (\text{Equation 3.1})$$

The water retention value test may be modified to model different water removal conditions for specific forming and pressing conditions. A reduction in the WRV value translates into a decrease in the water load entering the dryer section. Earlier work in the literature demonstrated a general relationship between the laboratory water retention value and the water content of a sheet of paper leaving the press section of a paper machine (Jayme 1958, Thode 1960, Abson 1980, Busker 1984). Specifically, Figure 3.4 (Busker 1984), semi quantitatively relates the WRV with the sheet dryness exiting the press section of a paper machine.

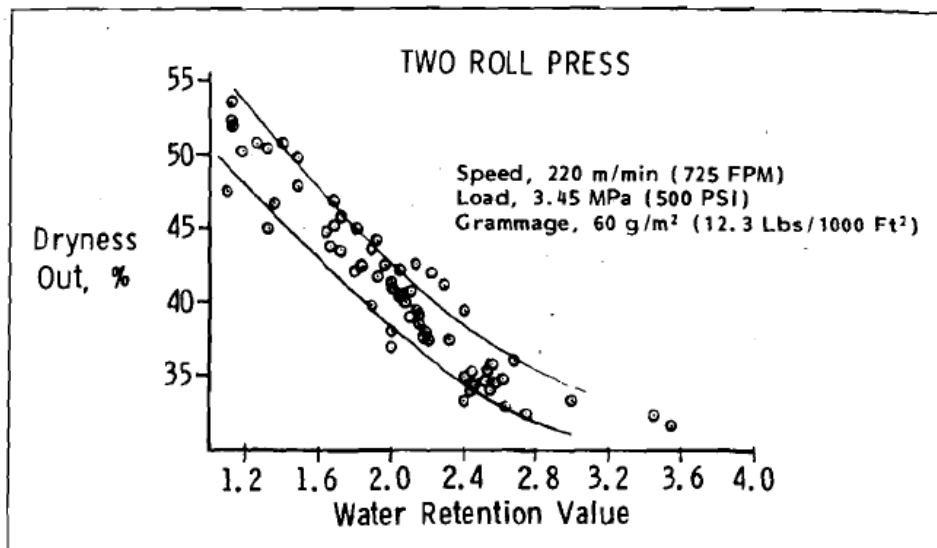


Figure 3.4. Dryness out of the press section of a paper machine versus the water retention value. (Busker 1984)

In the present work the TAPPI UM 256 water retention value test was utilized to determine the effect of chemical addition at varying dosages on sheet dewatering. Fiber (40 grams) was disintegrated for seven minutes in one liter of tap water (~50 - 60°C) in a TAPPI disintegrator to form a 4 wt% pulp slurry. Samples were then centrifuged in a Fisher Scientific Marathon 10K centrifuge at 900 G for 30 minutes in a brass open bottom crucible with a brass mesh supporting the fiber mat to mimic the forming and pressing section of a two press Fourdrinier machine. Samples were subsequently weighed on an Ohaus Explorer analytical balance (model E04130) and placed in Fisher Scientific Isotemp Standard Oven at 105°C overnight to remove all retained water prior to recording the final dried fiber weight.

3.2.2. Additional Pulp Testing

3.2.2.1. Surface Tension

Surface tension testing was performed to evaluate the potential effects of each additive as a function of system dosage. A KSV Instruments Sigma 70 surface tensiometer equipped with a platinum-iridium du Noüy ring was employed. Surface tension was calculated from measurements of ten surface oscillations. Measurements were recorded in DOS based software and were reported in dynes. Samples were prepared by using an Eppendorf model 5804R centrifuge to separate the fiber from the supernatant via centrifuging at 5000 rpm for 10 minutes in 60 mL Nalgene centrifuge tubes. The supernatant was tested in 10 cm standard dishes.

The du Noüy ring was cleaned in between samples by rinsing with distilled water and flaming to remove any remaining organics.

3.2.2.2. Charge Demand of the Pulp Slurry

The most common technique employed in the paper industry for measuring the charge of particulate suspensions is the streaming potential measurement in conjunction with polyelectrolyte titration. In this technique, a piston moves the slurry of interest back and forth through a narrow gap at a proprietary frequency. The motion produces an AC current between two electrodes contained in the measuring cell wall. Charged material adsorbed to the cell wall will be separated from its counter-ions by the flow of the slurry to create a streaming current which is reported as the streaming potential value. When this measurement is used in conjunction with polyelectrolyte titration, it is possible to determine the charge demand of the pulp suspensions by titrating the solution to a neutral charge with the appropriate cationic or anionic polyelectrolyte. An inherent assumption of the method is that the oppositely-charged polyelectrolyte forms a one-to-one charge complex with the charged particles of the system. The quantity of polyelectrolyte consumed at the point of charge reversal is referred to as the charge demand of the suspension. (Scott 1996). In the present work these measurements were performed with a Mutek Particle Charge Detector PCD-03. The two titrants used were cationic 0.001N poly-DADMAC by BTG, and anionic 0.001N PVSK also by BTG. All testing was performed with a 10 mL sample of pulp supernatant, in triplicate.

3.2.2.3. Attenuated Total Reflection Infrared Spectroscopy

Infrared spectroscopy is a powerful tool for the analysis of the molecular composition of a given material. Many sampling configurations exist for infrared spectroscopy, however, for bulk materials that absorb strongly in the infrared spectral region, options are limited. One technique that has found great utility in the measurement of strongly absorbing materials is Attenuated Total Reflection FT-IR (ATR-IR). The technique passes an infrared beam through an internal reflection element (IRE) with a higher refractive index than the sample medium, the beam is aligned such that it has an incident angle at the IRE/medium interface that is greater than the critical angle. Upon reflection from the interface an evanescent wave is generated that penetrates into the optically rarer medium for a distance of approximately the wavelength of the incident beam. (Harrick 1967) If the medium is IR adsorbing in the wavelength range of the evanescent (and incident) beam, then the reflected beam is attenuated accordingly. Measurement of the intensity of the reflected beam thereby provides an infrared absorbance spectrum of the interfacial region of the medium (Neivandt 1998).

ATR-IR was employed in the present work to determine the solution concentration of the cationic surfactant CTAB in pulp supernatant by integration of the area of the resonances assigned to CTAB in the C-H stretching region (2000 – 3000 cm^{-1}). Due to the cationic nature of CTAB and its tendency to adsorb on anionic surfaces such as silicon IREs, the solution pH was decreased to be below the isoelectric point of the metal oxide form of silicon (pH 2.0) to avoid the deposition of CTAB on the IRE. The supernatant of the pulp was isolated from the fibers via

centrifugation as described in Section 3.2.2.1. Supernatant pH was lowered by the addition of 4 N hydrochloric acid. Attenuated total reflection infrared (ATR-IR) spectroscopy measurements were performed using an ABB Inc. FTLA2000-104 spectrometer with a twin mirror reflection accessory and flow cell equipped with a Si internal reflection element by Harrick Scientific.

3.2.2.4. pH

In the papermaking industry the machine wet end falls into two distinct pH categories, acid machines operating at a pH of $\sim 4 - 5$, and alkaline machines operating at a pH of $\sim 7 - 8$. Throughout the present work pulp pH was monitored to assess any potential impact on the normal operating conditions of the industry. The pH was monitored with a Corning Pinnacle 545 pH meter equipped with a plastic bodied refillable electrode.

3.2.2.5. Canadian Standard Freeness

The degree of pulp refining is known to affect the water holding capacity of a fiber (Busker 1984). A fiber which has been refined to a greater level will hold more water since refining pulp increases the fiber surface area due to fibrillation of the exterior of the fiber (Smook 2002). The degree of refining may be monitored by examining the rate of water drainage from a pulp slurry sample and correlating this with the surface area of fibers within the slurry, this is known as a freeness measurement. The Canadian Standard Freeness test, TAPPI method T-227, is one such method and is commonly used to evaluate pulps in the paper industry. In the present work a Green's Slowness Tester wall model by the Star Brass Manufacturing

Company was employed to measure the Canadian standard freeness (CSF). The tester is comprised of a drainage chamber and a rate measuring funnel which allows water to exit via gravity while collecting a fiber mat on a screen. The “freed” water is collected in a 1000 mL graduated cylinder; where the volume collected is reported as the CSF in mL. A pulp with little surface area will drain water rapidly through the screen, and result in a large volume (700 mL or more) of water collected. However, if the same pulp was subjected to refining, the increased surface area of the fibers would cause water to drain much more slowly and the total volume of water collected would be greatly reduced (e.g. 100 – 200 mL). In the present work, this method was employed to prepare pulps for a pilot machine trial which had nearly identical drainage rates.

3.2.2.6. Thermogravimetric Analysis

To complement work investigating water removed in the forming and press sections, the energetics of water removed in the drying section was studied. To explore the rate of water removal by heat application, a TA Instruments 2950 TGA was employed to perform thermogravimetric analysis of pulp samples. The furnace of the instrument was electronically heated to the target temperature of 110°C, from which point the experiment was run isothermally. Dry nitrogen gas was used to sweep volatiles removed from the sample at a flow rate of 35 mL/min. Platinum sample pans, which held approximately 100 mg of sample, were employed. The experiment was run until the weight change of the sample over ten seconds was

negligible. Data was collected via a computer and analyzed with the TGA 2950 software package.

3.2.2.7. Contact Angle

A contact angle device was designed and built to facilitate imaging of the water contact angle within a glass capillary, and to measure the height of the water column within the capillary. By use of complementary surface tension data, a comparison between measured capillary forces and those predicted by the Young-Laplace equation was possible. The instrument allowed for images to be taken and for the head pressure of the capillary to be varied. A Cannon Rebel Xsi DSLR camera with a macro lens combination provided 12x optical magnification which permitted the use of Image J software to measure the resultant contact angles. Glass capillaries (0.75mm internal diameter) were cleaned using a 20wt% Contrad 70 detergent solution, followed by nitric acid to remove organic contaminants. Capillaries were imaged in situ by placing the lower end of the capillaries vertically in troughs containing solutions of 18.2 M Ω -cm water and 1mM, CTAB side-by-side.

3.2.3. Paper Testing

3.2.3.1. Handsheets

Handsheets are bench scale formed sheets of paper which allow physical testing to be performed on a representation of a full scale commercial sheet. Handsheets were formed using a modified version of TAPPI Method T205 Forming Handsheets for Physical Testing of Pulp. Utilizing 4wt% consistency pulp prepared in the TAPPI Disintegrator for seven minutes, 150 gm/m² handsheets were

produced as recommended by Appendix B in T205 to mimic paperboard sheets. The choice to make paperboard type handsheets was made in order to find a middle ground between fine paper production and the production of ceiling tiles. The sheets were formed in a Herman Manufacturing Company handsheet mold and pressed in a Herman Manufacturing Company handsheet press. The resulting sheets were air dried and stored in a controlled temperature and humidity room over night before testing was performed. The room was set to TAPPI T402 conditioning specifications of $50.0\% \pm 2.0\%$ relative humidity and $23.0^{\circ}\text{C} \pm 1.0^{\circ}\text{C}$.

3.2.3.2. Bulking

A visual increase in WRV pad thickness apparent under certain experimental conditions prompted the measurement of the thickness of the relevant pads. Measurements were performed utilizing a Pittsburg 6" digital caliper. Three pads per sample condition were measured twice to generate statically valid thicknesses of the WRV pads.

3.2.3.3. Sheet Caliper

Sheet caliper was measured since it is a critical property that many manufactures utilize to sell their products. In addition sheet caliper was monitored to determine if the bulking trend observed in the WRV pads translated to sheets formed by other processes. Utilizing TAPPI Method T-411 and a TMI dead weight caliper, the sheet caliper of both handsheets and pilot trial produced paper was measured.

3.2.3.4. Sheet Formation and Floc Distribution

The Kajaani formation tester utilizes light transmittance to characterize sheet uniformity, a commonly examined parameter in papermaking quality control. A high Kajaani value is indicative of the following sheet characteristics: improved formation, increased density, heavier basis weight, and decreased filler content for a specific basis weight. Generally, the higher the Kajaani value, the lower the sheet porosity, as the sheet has become “closed.” An additional forming parameter commonly reported is the floc distribution in units of flocs/cm²; the larger the floc distribution number the smaller the average floc size. In the present work a standard Kajaani formation tester with Valmet Automation formation analyzer V 1.2 software was employed.

3.2.3.5. Tensile

The tensile strength of paper is dictated by factors such as fiber strength, fiber length, and the extent of fiber-fiber bonding. Tensile strength is a commonly employed parameter used for quality control purposes since it is easily measured and is an excellent indication of the serviceability of many papers. In addition, tensile strength may be used as an indicator of potential resistance to web breaking of papers, such as printing papers, during printing on a web fed press or other web fed converting operation. In the present work the tensile strength of handsheet and pilot trial sheet samples was evaluated via TAPPI Method T-494 utilizing a constant-rate-elongation testing machine which applied an elongation rate of 25 mm/minute. Specifically, an Instron 5564 was employed to measure machine direction and cross

machine direction sheet tensile. Samples were prepared by cutting 25mm wide strips approximately 220mm long utilizing a TMI tensile sample cutter. A total of 10 samples were run for each condition to generate a statistically relevant average.

3.2.3.6. Burst

A measure of physical sheet strength that complements tensile measurements is burst strength. TAPPI method T-403 states that the bursting strength of a sheet is the maximum hydrostatic pressure required to rupture the sheet when a controlled and constantly increasing pressure is applied through a rubber diaphragm to a circular area, 30.5 mm (1.20 in.) in diameter. A Lorentzen and Wettre Burst-O-Matic was employed in the present work to perform the burst test. Samples were tested in six locations across a given sheet to provide statistically meaningful data.

3.2.3.7. Internal Bond

A measure of the internal bond strength of a sheet is known as the I-Bond or Scott bond test. TAPPI method T-569 Internal bond strength (Scott type), defines the test as a measure of the energy required to rapidly delaminate a sheet-type specimen. "Z" directional rupture is initiated by the impact of a pendulum having both a controlled mass and a controlled velocity that exceeds 6000 times the velocity of tensile strength and other dead-weight testers. A TMI I-Bond Monitor / Internal Bond 80-01 tester was employed along with a TMI I-Bond preparation station.

3.2.3.8. Fiber Ash Content

The ash content of WRV pads was determined by employing TAPPI method T-211 Ash in wood, pulp, paper and paperboard: combustion at 525°C. T-211 ash test were performed by oven drying a fiber sample in a Fisher Scientific Isotemp Standard Oven at 105°C for 20 minutes, prior to placing the sample in a ceramic crucible. An initial weight was recorded on an Ohaus Explorer analytical balance (model E04130) and the sample placed in a Thermolyne 62700 Furnace at 525°C for two hours. The resulting chars were weighed and divided by the initial weight to determine the ash content of the sample.

3.2.3.9. Hydroxyl number

Hydroxyl number determination was performed on paper samples that were oven dried at 105±2°C to ensure complete moisture removal. Dry paper sheets of 1.50±0.05g were analyzed according to Method A of ASTM D4274-05 Standard (ASTM 2005). The standard method, primarily used for determining hydroxyl numbers of polyols, was adapted with a slight modification: instead of the specified 20mL of acetylation reagent mixture, 50mL was employed. The stock acetylation reagent mixture was comprised of 127mL of acetic anhydride and 1000mL of pyridine. This modification was made due to the need for a sufficient quantity of the acetylation reagent to ensure reaction of all available hydroxyl groups on the fiber. The acetylation reagent was added to the fiber sample in a 98±2°C water bath. The reaction was allowed to proceed for two hours after which the number of hydroxyl groups that had reacted was quantified from the concentration of acetic acid,

generated as a side product of reaction. The concentration of acetic acid was determined by titration with sodium hydroxide. The hydroxyl number in mg KOH/g sample was subsequently calculated via:

$$\text{The Hydroxyl Number: } [(B-A) \times N \times 56.1] / W$$

Where, A is the volume (ml) of sodium hydroxide solution required for the titration (after the phenolphthalein reaction) of the liquefied sample; B is the volume (ml) of sodium hydroxide solution required for titration of the blank (control) solution; N is the normality of the sodium hydroxide solution; and W is the weight of the fiber sample. Results are reported in the ASTM accepted standard of mg of potassium hydroxide, which is why the molar mass of potassium hydroxide (56.1) is included in the equation. Three samples from each condition were tested to provide a statistical average hydroxyl number.

3.2.3.10. Mercury porosimetry

Mercury porosimetry is a technique commonly used to characterize the porosity and pore structure of materials via application of various levels of pressure to a sample immersed in liquid mercury. Pore size may be determined with knowledge of the external pressure required to force the mercury into a pore against the opposing force of the mercury's surface tension. A force balance equation known as the Washburn equation may be computed for a material having cylindrical pores:

$$P_L - P_G = \frac{4\sigma * \cos \theta}{D_p}$$

Where P_L is the pressure applied liquid mercury for intrusion, P_G is the pressure within the sample prior to the intrusion of mercury (as the measurement commences at a vacuum this value is generally 0.5 psia), σ is the surface tension of mercury, θ is the contact angle of mercury (the contact angle of mercury with most solids is between 135° and 142° , so an average of 140° is employed) and D_p is the pore diameter. In the present work porosimetry was employed to examine changes in the pore structure of WRV pads, and paper samples as a result of additive addition. Samples were prepared by cutting a portion of WRV pads or paper sheets weighing $0.200 \text{ g} \pm 0.002 \text{ g}$ and placing them in 5cc penetrometer. Measurements were performed with Micromeritics Autopore IV instrument over a pressure range of 0.50 psia to 25,000 psia. Duplicates were run to confirm results.

CHAPTER 4

BENCH SCALE INVESTIGATIONS OF CHEMICALLY ENHANCED WATER REMOVAL

4.1. Introduction

Decreasing the water load entering the drying section of a paper machine, and/or decreasing the energy required to evaporate the residual water, is expected to result in significant energy and hence fiscal savings. As described in Chapter 2 the vast majority of efforts made to increase the amount of water removed in the forming and pressing operations to date have focused on mechanical methods. Specifically, most work has centered on examining means of extending the pressure impulse, improving fabric and roll design, and introducing new machine configurations. An alternative and little explored methodology is to reduce the hydraulic force required to overcome the capillary force holding water within the fiber walls and between fibers, through reduction of the magnitude of the capillary force itself. Additionally, the concept of modifying the energetics of water bonding to cellulose to reduce the thermal energy required to evaporate bound water has not been pursued.

The fundamental parameters that govern water removal from capillaries within fiber walls and between fibers are known and were reviewed in Section 2.6.2. Specifically, the relevant parameters are given by the Young-Laplace equation and are; the water/air surface tension, the cellulose/water contact angle, and the pore radius. Surfactants are known to adsorb onto cellulose (cationic surfactants in

particular) and hence affect the surface energy, and consequently the contact angle. Additionally, surfactants modify the water/air surface tension. Thus, at least two of the relevant parameters may be positively modified through judicious application of surfactants. Consequently the present work aimed to investigate, from both a fundamental and an applied perspective, the effect of surfactant addition on the dewatering of paper in the formation and press sections, and the energetics of residual water removal in the dryer section. Bench top testing was employed to provide a platform for the rapid screening of additives, as well as to examine the physical properties of the resulting paper.

4.2. Experimental Results

4.2.1. WRV Exploration

Utilizing the TAPPI UM 256 water retention value test, the effect of cetyltrimethylammonium bromide (CTAB) addition at varying dosages was observed by pulping 40 grams of fiber in one liter of tap water (~50 - 60°C) in a TAPPI disintegrator to form a 4 wt% pulp slurry. CTAB was added as a dry powder to the water at the commencement of the disintegration (here in after referred to as pulping) process, prior to the addition of fiber. Figure 4.1 presents a plot of WRV vs. dosage of CTAB (g/g of paper) for a 7 minute pulping duration employing unprinted recycled paper. The following dosages of CTAB were tested: 0 g (control); 0.35 wt% , 0.70 wt% , 1.0 wt% , 1.75 wt% , and 3.5 wt% on a dry fiber basis. Each data point represents an average of six separate WRV samples and the error bars represent 95% confidence intervals based on six data points at each CTAB dosage.

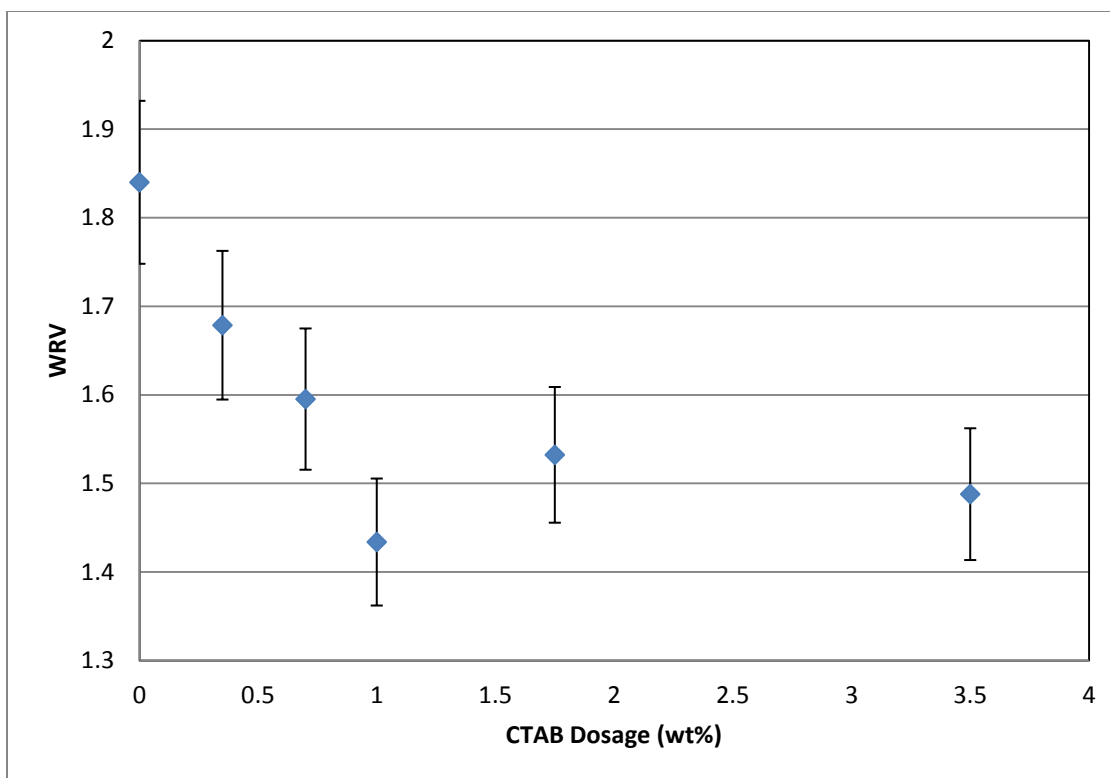


Figure 4.1. WRV versus CTAB dosage for unprinted paper.

It is evident from Figure 4.1 that as the amount of CTAB increases, the WRV decreases. A 1 wt% dosage of CTAB results in a WRV decrease of over 20% in relation to the control. It appears that the system reaches a saturation point at, or just beyond, the 1 wt% dosage, suggesting a maximum functional dosage of 1wt%.

A decrease in the WRV of 20% is a major gain in water removal efficiency. If one employs Figure 3.4 (Busker 1984), a WRV value of 1.85 (as seen for the control in Figure 4.1) corresponds to a solids content of approximately 43wt% out of the press section. The addition of 1 wt% CTAB reduced the WRV to a value of 1.50, which corresponds to solids content out of the press section of approximately 47 wt%, a 4 wt% increase over the control. By performing a mass balance around the dryer section of a hypothetical paper machine, this increase of the solids out of the

press section (4 wt%) can be translated into a percentage of water reduction requiring removal in the dryer section.

Examining a hypothetical paper machine as presented in Figure 4.2 with a width of 25 ft, running at 3000 ft/min, at a basis weight of 0.01 lb/ft², the following calculation is performed.

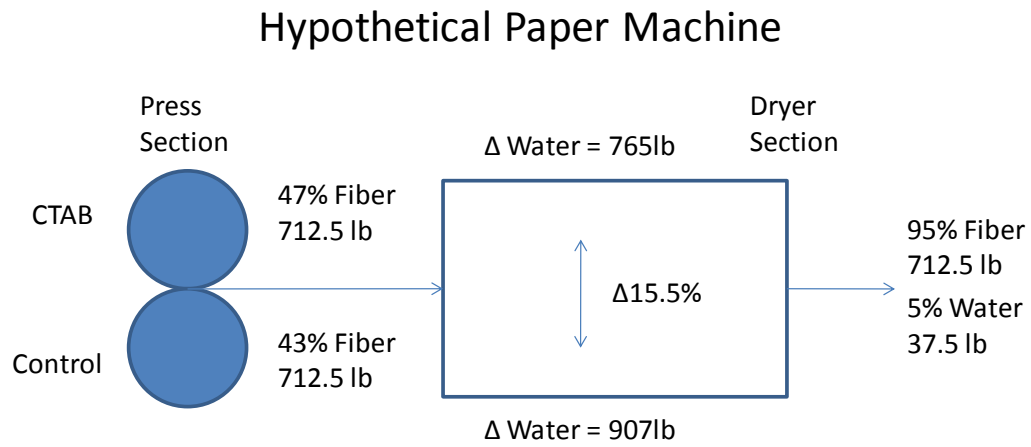


Figure 4.2. Hypothetical paper machine with mass balance.

The total production of the machine is calculated to be 750 lb/min of finished paper. Estimating the average finished sheet moisture to be 5 wt% (i.e. a solids content of 95 wt%), then the solids out of the dryer section of the machine is 712.5 lb/min and the water out of the dryer section is 37.5 lb/min. A mass balance may then be performed around the dryer section to calculate the amount of water removed by the dryer section, which in turn may be used to calculate the energy savings derived from the higher press solids as estimated by the WRV test. For the control condition it was determined that the solids content out of the press section was 43%. Given that the fiber mass is 712.5 lb/min, the water content (57%) must be 944.5 lb/min. The water removed in the dryer section is consequently 944.5-

37.5 lb/min, which is 907 lb/min. For 1 wt% addition of CTAB it was determined that the solids content out of the press section was 47%. Given that the fiber mass is 712.5 lb/min, the water content (53%) must be 802.4 lb/min. The water removed in the dryer section is consequently 802.4-37.5 lb/min, which is 765 lb/min. The percentage difference in water removed in the dryer section between the control and the CTAB addition case is 907-765 lb/min, which is 142 lb/min, or 15.5%. The corresponding energy savings is determined employing the heat of vaporization of water (970 BTU/lb) to be 137,740 BTU/min. It should be noted that if the machine was running at its maximum dryer capacity, the reduction of water load in the dryer section of 15.5% could be employed to enable a total production increase of 15.5%. This conclusion derives from the assumption that the unused dryer capacity could be utilized if the machine speed was increased proportionately, thereby increasing the water load in the dryer section to match the control water load.

From the above calculations it may be seen that the difference observed in the WRV value ($1.8-1.4=0.4$) may be multiplied by a factor of 10 to derive the difference in solids out of the press section in weight percent ($0.4 \times 10 = 4$) which may in turn be related to the approximate percentage difference in water removed in the dryer section by multiplying by a factor of 4 ($4 \times 4 = 16$).

Figure 4.3 presents WRV data obtained from a comparable experiment to that presented in Figure 4.1, with the exception that printed paper was employed, and a lower dosage range of CTAB was utilized.

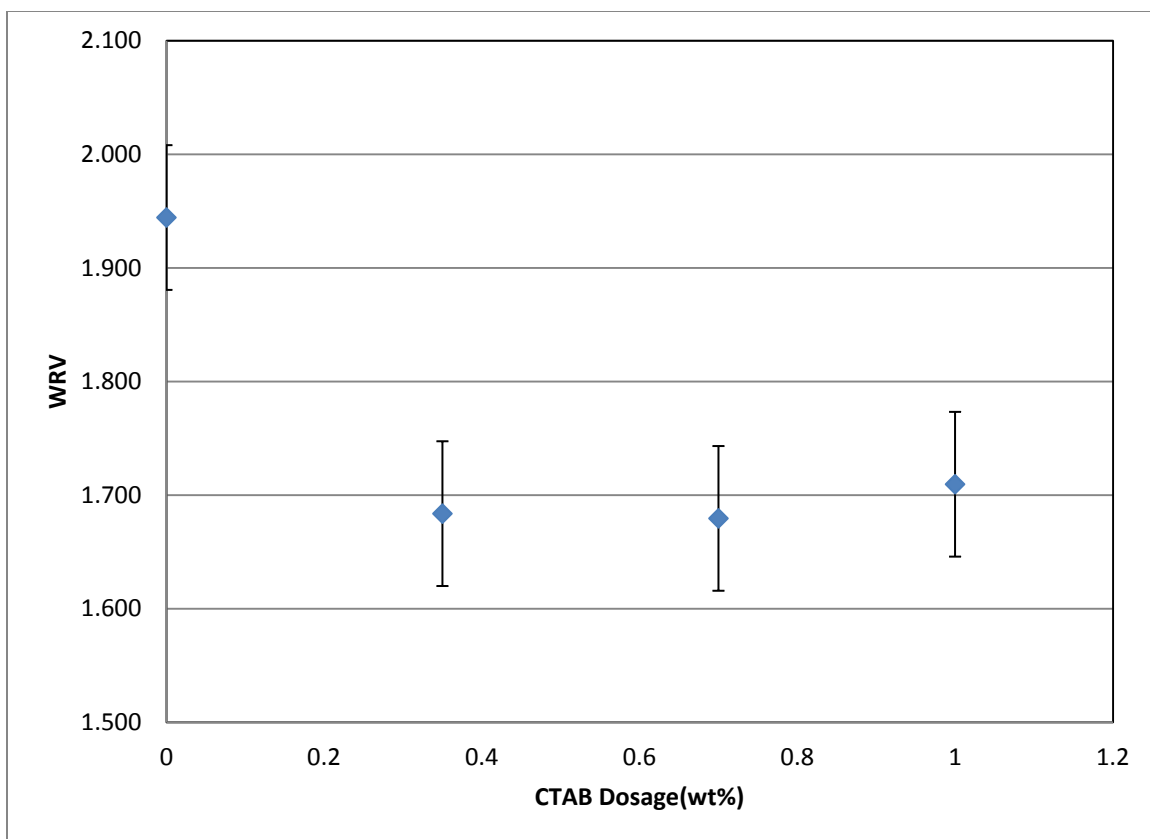


Figure 4.3. WRV versus CTAB dosage for recycled newsprint. A maximum WRV decrease of 15.0% is observed at 1wt% CTAB.

From Figure 4.3 it is determined that for printed paper, the WRV is decreased by approximately 15% by the addition of 1 wt% CTAB. As printed paper contains more ionic trash, i.e. ink, a portion of the cationic surfactant is likely attracted to the ink rather than to the cellulose surface or the air/water interface, thereby causing a smaller change in the WRV relative to that found in the unprinted case of 20%.

Pulping time was varied from 7, 10, 15 to 30 minutes with no statistical changes in the WRV trend as a function of CTAB dosage being noted, as may be seen in Figure 4.4.

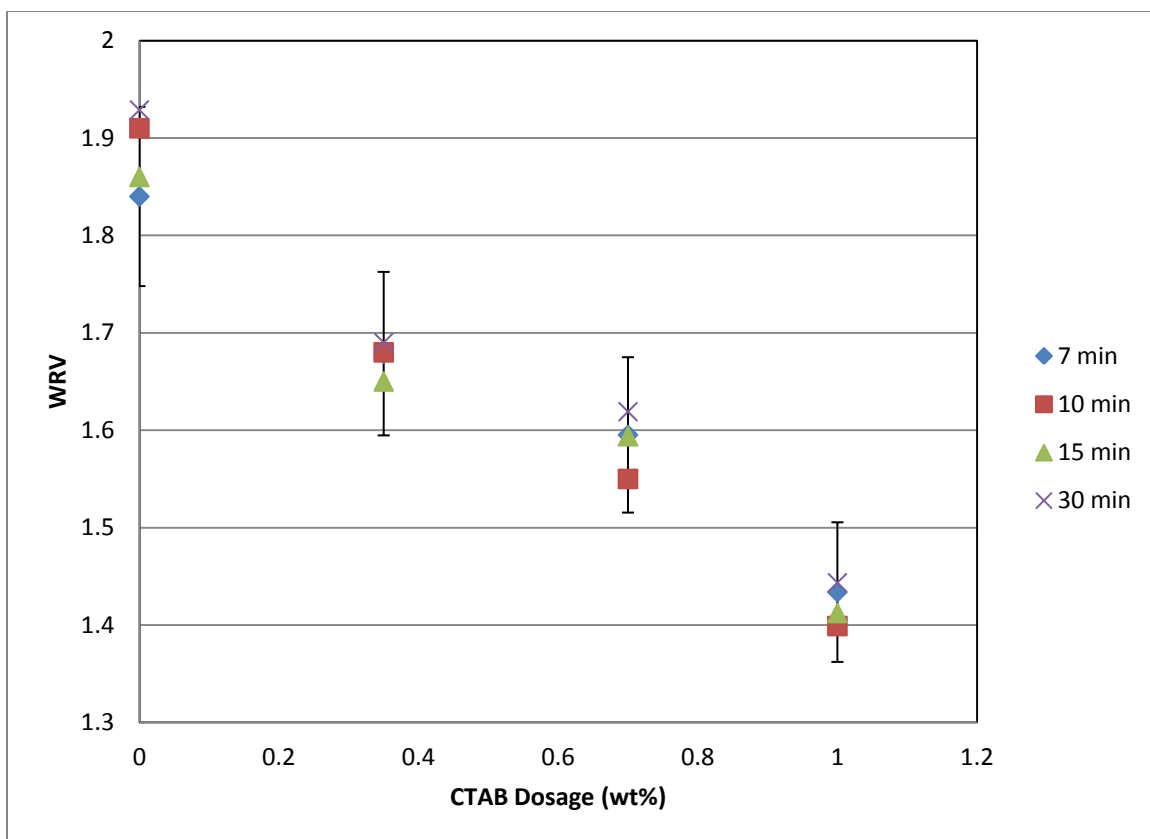


Figure 4.4. WRV versus CTAB dosages for varied pulp times of unprinted paper.

4.2.2. Pulp Testing

In order to determine the breadth of applicability the apparent water retention effect of CTAB would have on the paper industry, several types of pulps were evaluated via the WRV test at CTAB of dosages of 0.35 wt%, 0.70 wt%, and 1.0 wt% in a 7 minute pulping time. Specifically, experiments were performed on; recycled directory, sulphite fibers, Sappi Co-pulp, single side coated (C1S) broke, non-bleached softwood kraft (NBSK) and brown recycled fiber pulps, and are presented in Figures 4.5 – 4.10 respectively. The data indicates that regardless of the pulp type or source, a trend of a reduction in the WRV with increased CTAB dosage is observed. Control WRV values for the pulps ranged from 1.65 to 2.05

while the minimum WRV, commonly observed at 1wt% CTAB dosage, ranged from 1.32 to 1.63, representing a percent decrease in the WRV ranging from 13.9% to 22.6%.

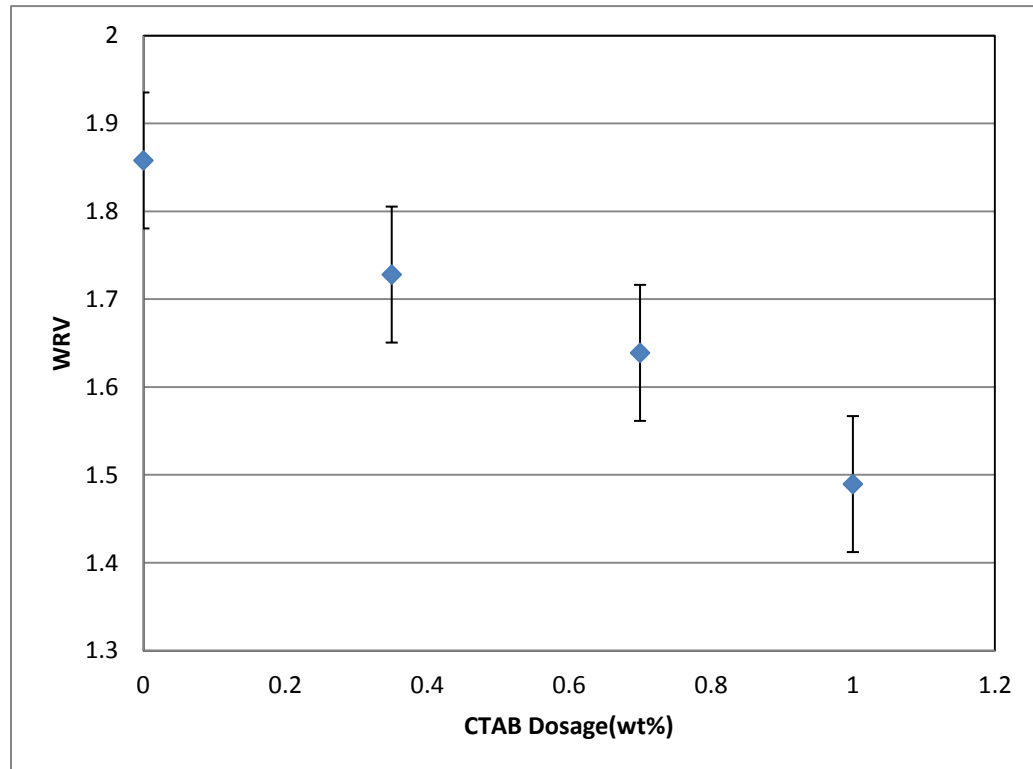


Figure 4.5. WRV of recycled directory as a function of CTAB dosage. A maximum WRV decrease of 19.8% is observed at 1wt% CTAB.

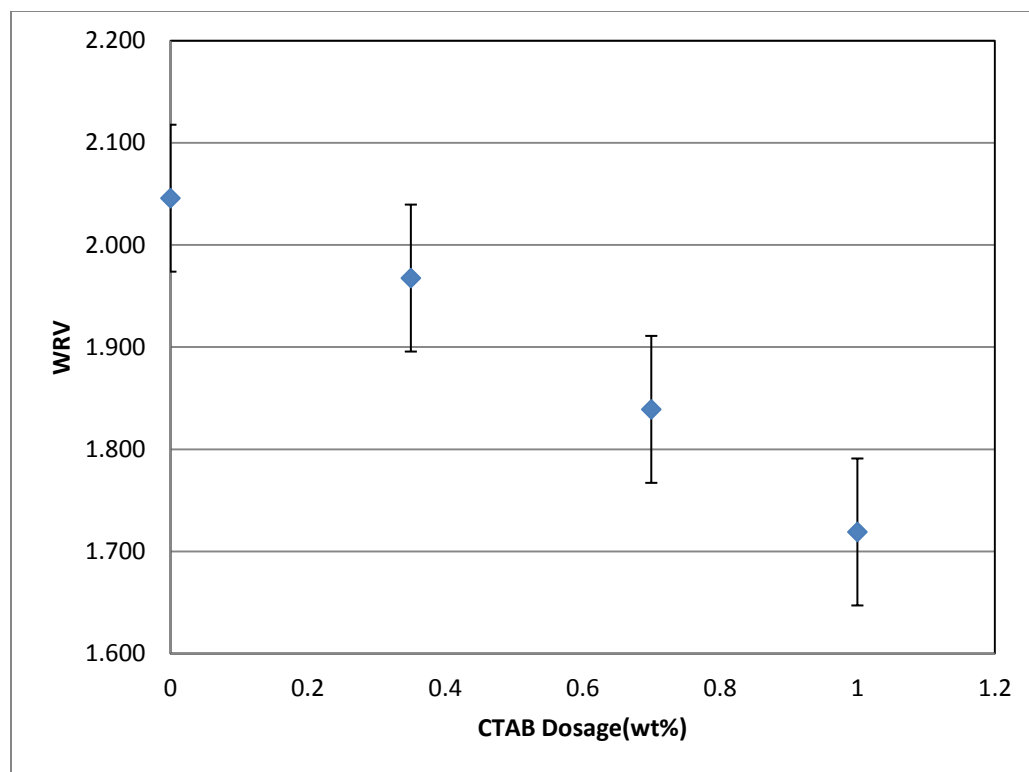


Figure 4.6. WRV of sulphite fiber as a function of CTAB dosage. A maximum WRV decrease of 16.0% is observed at 1wt% CTAB.

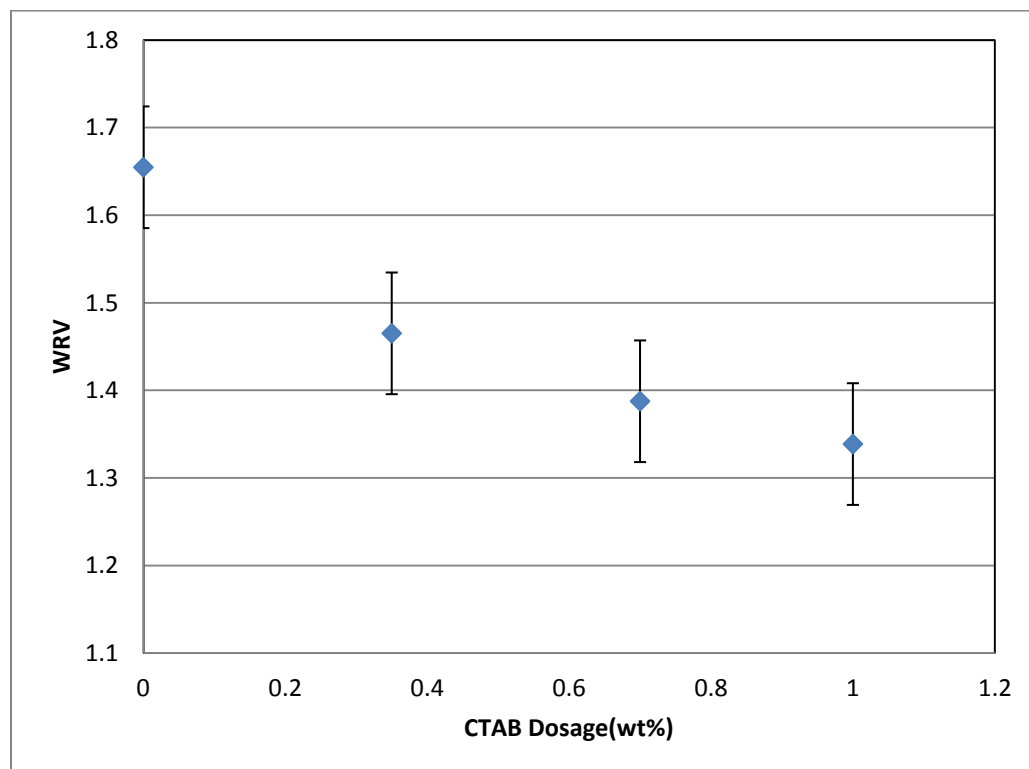


Figure 4.7. WRV of Sappi Co-pulp as a function of CTAB dosage. A maximum WRV decrease of 19.1% is observed at 1wt% CTAB.

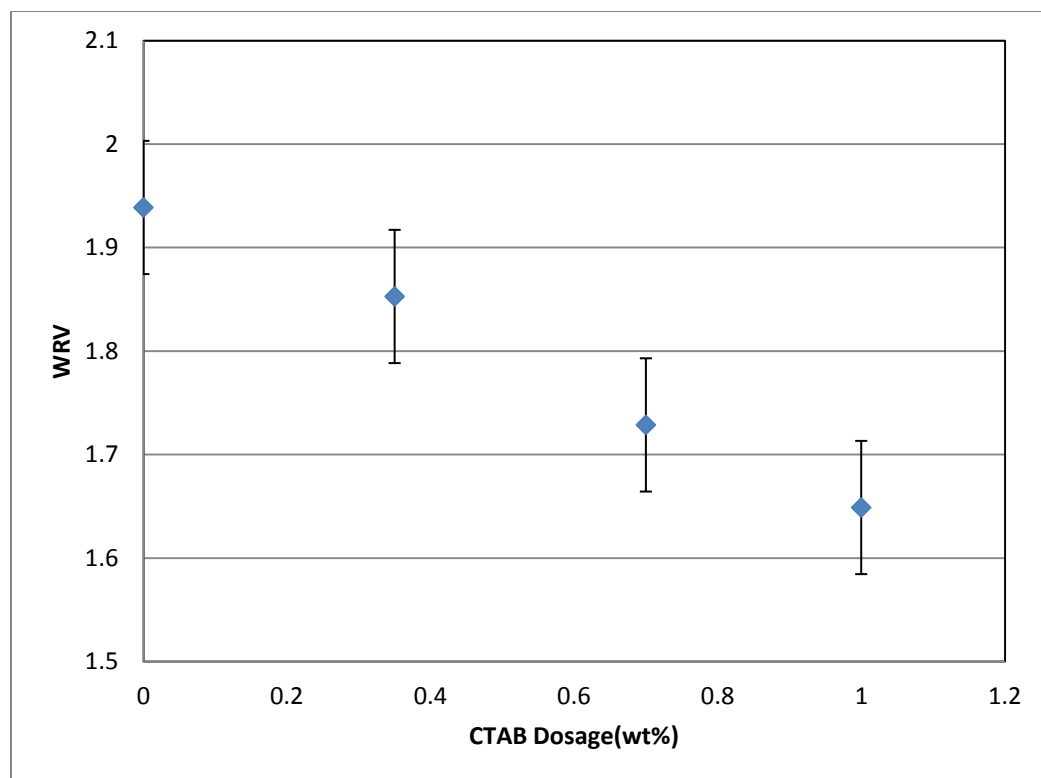


Figure 4.8. WRV of C1S broke as a function of CTAB dosage. A maximum WRV decrease of 15.0% is observed at 1wt% CTAB.

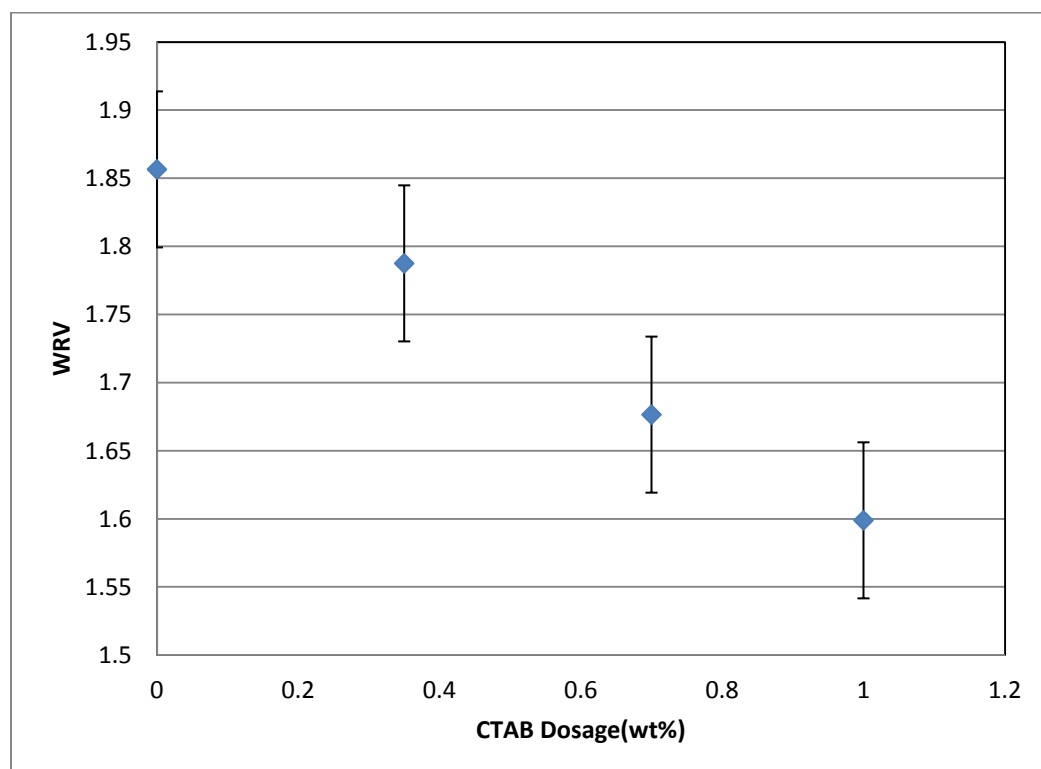


Figure 4.9. WRV of NBSK as a function of CTAB dosage. A maximum WRV decrease of 13.9% is observed at 1wt% CTAB.

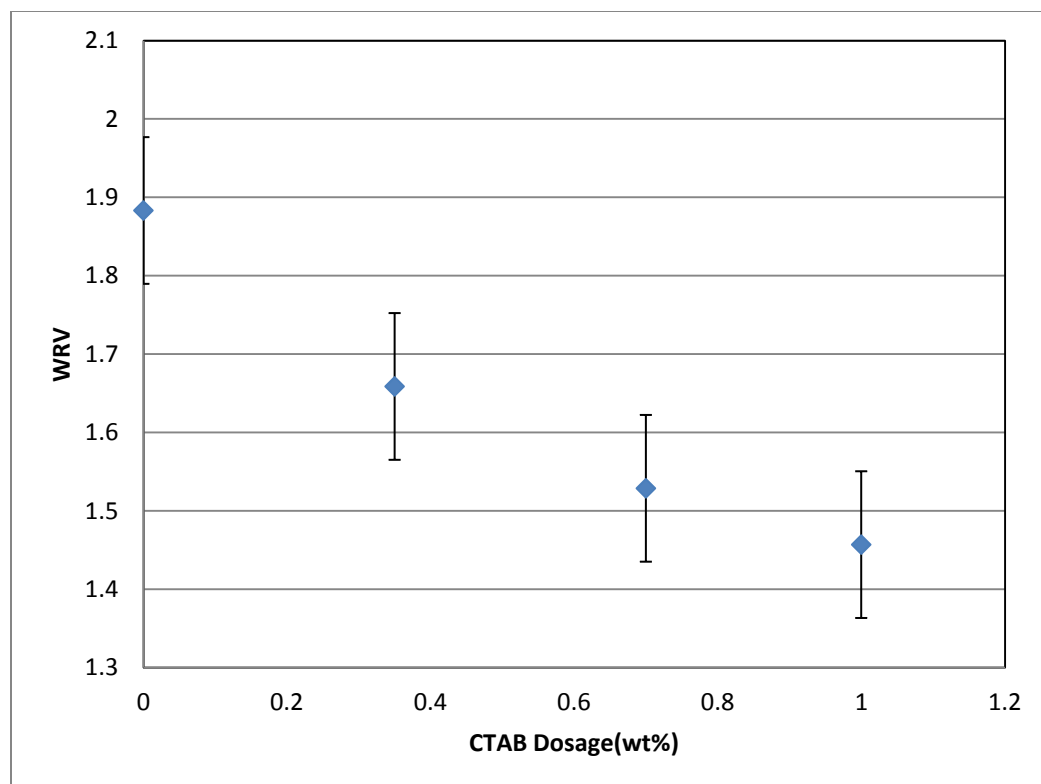


Figure 4.10. WRV of unbleached brown recycled fiber as a function of CTAB dosage. A maximum WRV decrease of 22.6% is observed at 1wt% CTAB.

It is evident from Figure 4.5 – 4.10 that the addition of CTAB to pulps comprising a wide variety of fibers enhances the extent of water removal in the forming and pressing operations as modeled by the WRV test. The effect varies to some extent depending on the fiber source, which is most likely due to the degree of fibrillation of the fibers and the resultant effect on the fibers' water holding capacity, in addition to any potential differences in the surface chemical characteristics of the fibers.

4.2.3. Additive Screening

A set of screening experiments was performed to measure the effectiveness of an assortment of additives on modification of the WRV in an attempt to identify

which parameters of the Young-Laplace equation were being manipulated by CTAB. Since CTAB is known to affect surface tension, a selection of other surfactants of differing head group charges and varying chain lengths was employed to evaluate what correlation, if any existed between WRV and surface tension. Since CTAB is a cationic surfactant, sodium dodecyl sulfate (SDS) and lignosulfonic acid, both anionic surfactants, and Triton X-100, a non-ionic surfactant, were included in the screening list.

In addition to probing a potential surface tension correlation, the opportunity was taken to examine additives previously described in literature as having effects on surface tension and/or WRV values, as well as an additive that anecdotal evidence had suggested affects the WRV. Specifically, the effect of a cationic polymer widely used as a retention aid, Percol 182, was examined to determine if the charged, cationic nature, of CTAB alone was the cause of the decreased WRV. Secondly, the effect of colloidal silica (Aerosil 380) was studied due to personal communications (Bilodeau 2007) stating that it is suspected of decreasing WRV values through lumen loading.

The additives were introduced into the water employed to create a 4 wt% pulp slurry of recycled unprinted fiber. The slurries were prepared by pulping approximately 40 grams of recycled fiber in one liter of warm tap water in a TAPPI disintegrator for seven minutes. Additives were employed at three levels; 0.35 wt%, 0.7 wt% and 1.0 wt%. WRV tests were performed immediately upon completion of pulping; a correlated surface tension measurement was made at the same time. Two additional surface tension measurements were made at sequential ten minute

intervals in order to study the time dependence of the surface tension of the pulp slurry. Surface tension measurements were performed as described in Section 3.2.2.1.

Figure 4.11 presents WRVs as a function of additive dosage for the control with no additive, CTAB, SDS, Triton X-100, Percol 182, Aerosil 380, and lignosulfonic acid. It may be seen from Figure 4.11 that the only additives that created measurable changes in the WRV were CTAB, SDS, lignosulfonic acid, and Triton X-100.

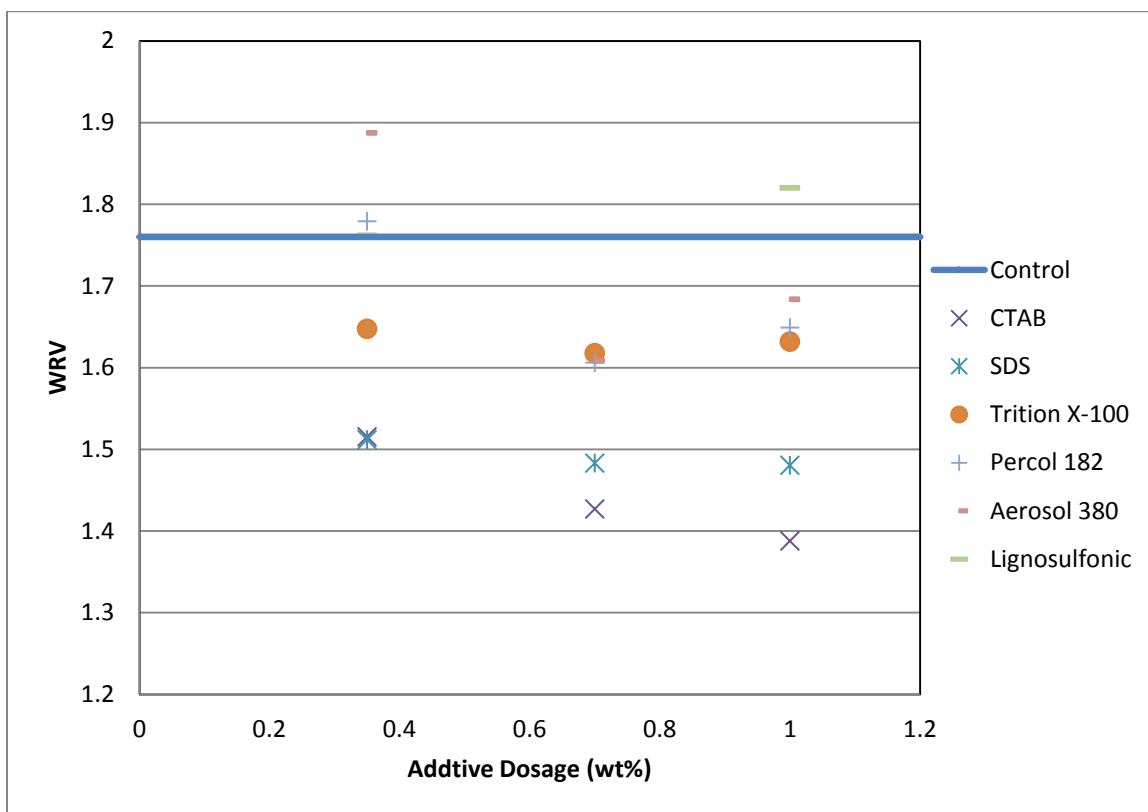


Figure 4.11. WRV versus dosage of CTAB, SDS, Triton X-100, Percol 182, Aerosil 380, and lignosulfonic acid.

It is evident from Figure 4.11 that the most effective additive at decreasing the WRV on a weight basis was CTAB. Indeed, the degree of effectiveness as a

function of dosage for the various surfactants had the following dependency CTAB>SDS>Triton X-100. Conversion of the data to molar basis resulted in an identical trend in surfactant effectiveness. It is noted that no significant decreases in the WRV were evident for any of the other additives.

Additional screening was performed with octadecyl trimethylammonium bromide (OTAB) and a generic alkyl trimethylammonium bromide mixture (Cetrimide), since both possess the quaternary ammonium head groups of CTAB, yet vary in chain length. Specifically, OTAB has an 18 carbon chain backbone while Cetrimide is comprised primarily of 14 carbon chain backbone structure. A statistically similar reduction in the WRV as a function of dosage of OTAB and Cetrimide was observed as that seen for CTAB, the resultant data is presented in Figure 4.12. At the higher dosages, CTAB appears to potentially outperform OTAB and Cetrimide; however the data is within statistical error.

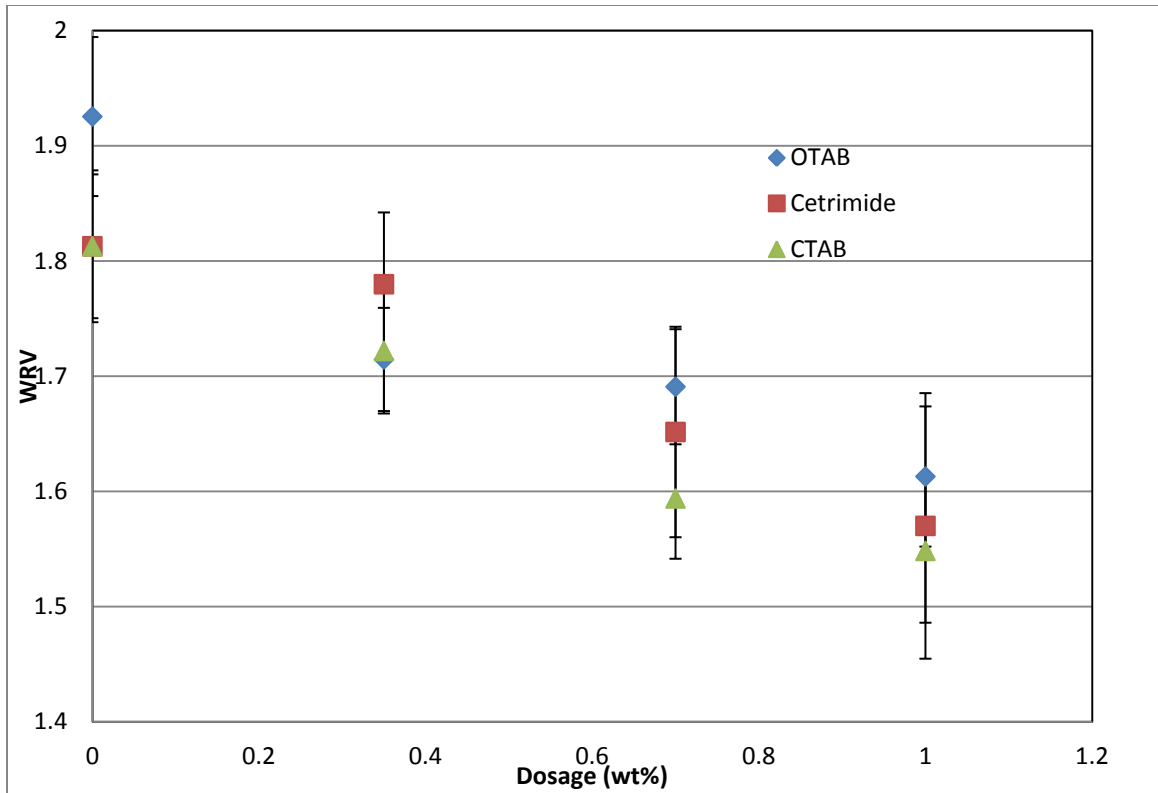


Figure 4.12. WRV versus various dosages of OTAB, Cetrimide, and CTAB.

4.2.4. Surface Tension Data

Figures 4.13 presents surface tension of the pulp slurries prepared with the various additives as a function of dosage; data are presented for the control (no additive), CTAB, SDS, Triton X-100, Percol 182, Aerosil 380 and lignosulfonic acid.

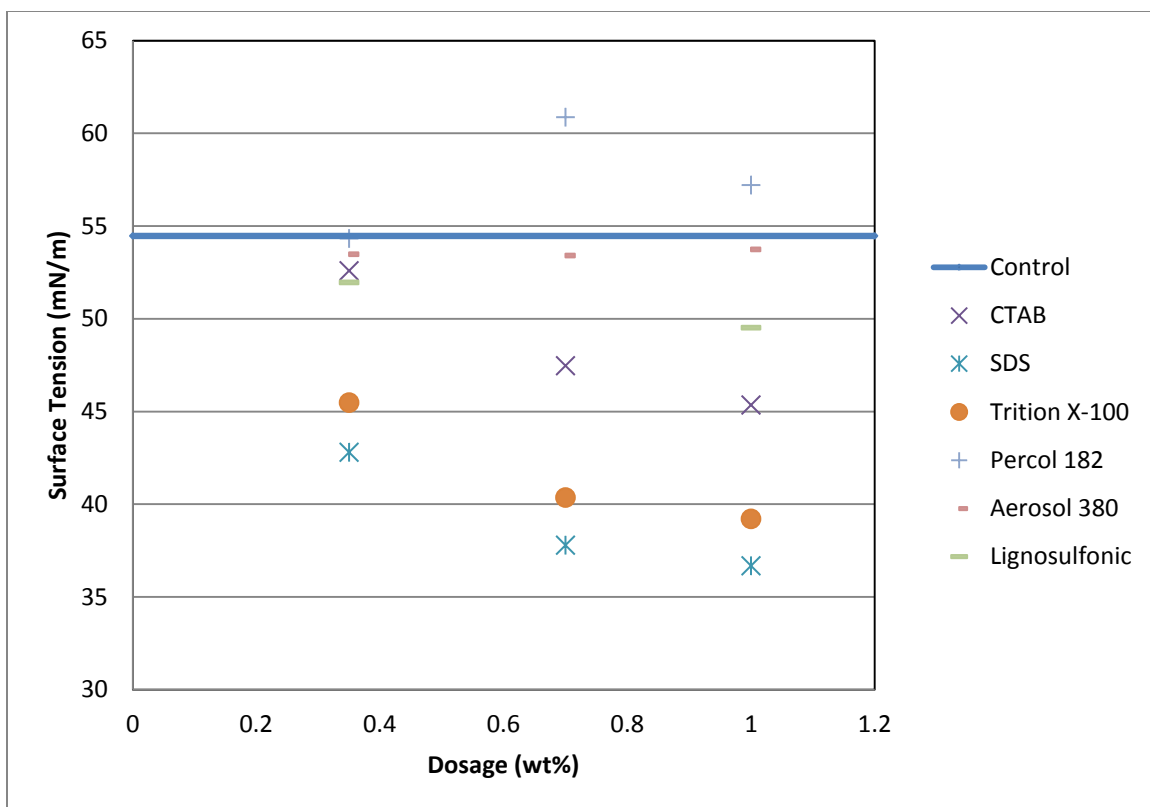


Figure 4.13. Surface tension versus dosage of CTAB, SDS, Triton X-100, Percol 182, Aerosil 380, and lignosulfonic acid.

It may be seen from Figure 4.13 that the only additives that give rise to a significant change in the surface tension were CTAB, SDS, lignosulfonic acid, and Triton X-100. The control line represents the average of three controls taken during the screening measurements. It is evident that all four surfactants decreased the surface tension with the degree of effectiveness as a function of dosage having the following dependency SDS>Triton X-100>CTAB>lignosulfonic acid.

The WRV data acquired in the screening process (Figure 4.12) are plotted as a function of surface tension of the most effective additives (Figure 4.13) in Figure 4.14.

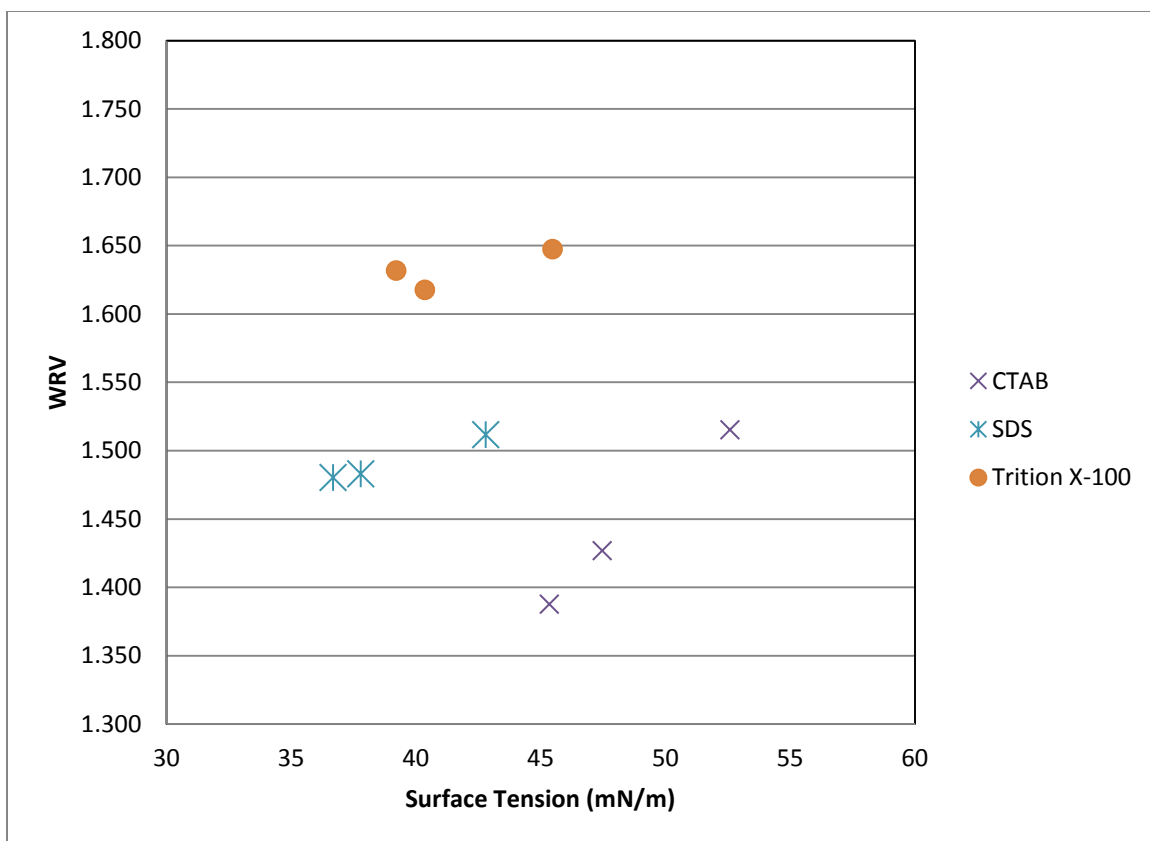


Figure 4.14. WRV versus surface tension of CTAB, SDS, and Triton X-100.

The Young-Laplace (Equation 2.2) predicts a linear trend of the reduction of capillary pressure with changes in surface tension. As such it is expected that the water retention should display a constant linear decrease with decreasing surface tension. It is noted that while the experimental data of Figure 4.14 do in fact depict linear decreasing trends of WRV with surface tension, the gradients vary for the different surfactant employed. In addition it is evident from Figure 4.14 the WRV decrease cannot derive solely from the surface tension change since SDS had the lowest measured surface tension, yet CTAB displayed the lowest WRV values. This result leads to the conclusion that there must be an additional parameter, or parameters, contributing enhanced water removal from the WRV pads in the presence of surfactant. Further, according to the Young-Laplace equation this

parameter, or parameters, must be the pore radius, the liquid/solid contact angle, or both. These parameters are explored in later experimentation.

4.2.5. Synergistic Affects of CTAB and SDS Addition

Given that at least a portion of the effectiveness for SDS and CTAB in lowering the WRV stems from modifying a parameter other than surface tension, an experiment was designed to examine if the two mechanisms are synergistic. A pulp slurry was prepared with 1wt% CTAB and WRV and surface tension measurements were performed employing a portion of it. The residual pulp was subsequently treated with 1wt% SDS and retested. Similarly, a second sample was prepared employing SDS as the initial additive with CTAB as the second additive. Figure 4.15 presents the resultant data from this experiment.

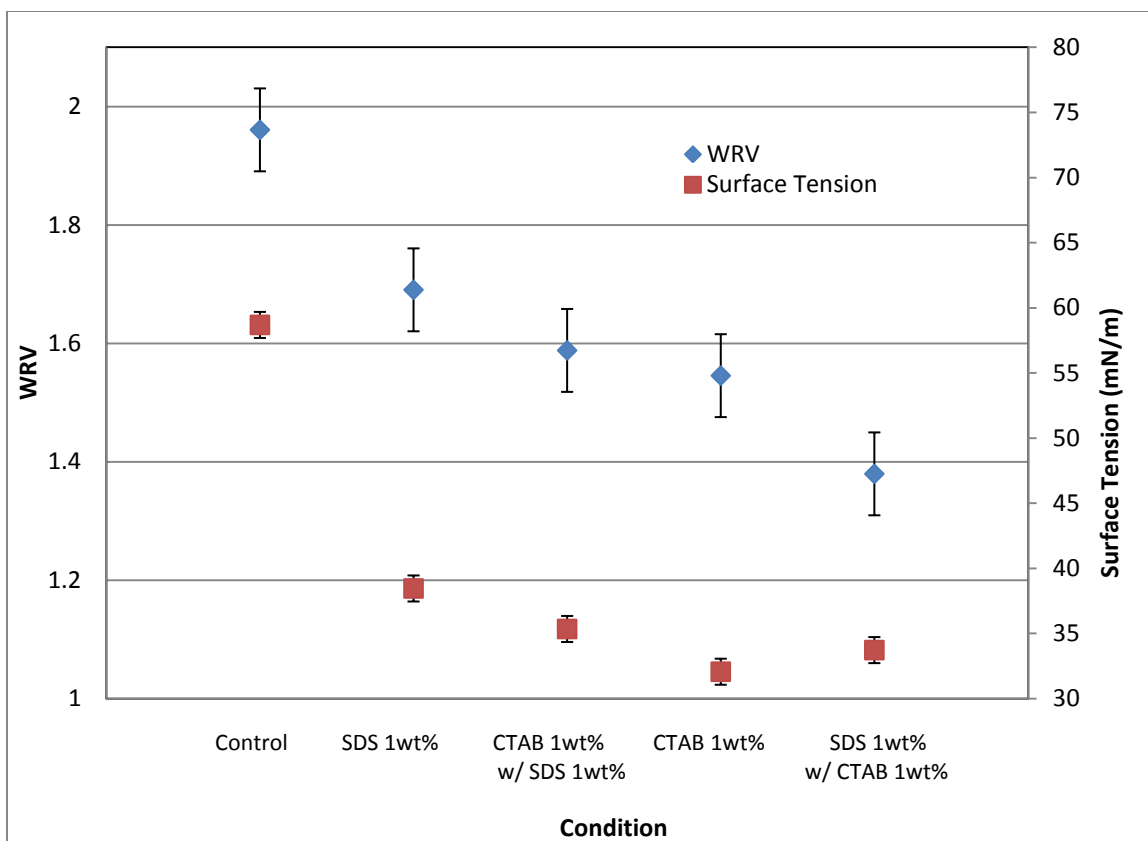


Figure 4.15. WRV (left axis) and surface tension (right axis) data for CTAB and SDS single and sequential addition.

Investigation of Figure 4.15 reveals that the reduction in the WRV obtained by each additive individually is increased when the second additive is incorporated. It is noted that while each initial additive lowers the surface tension, the second additive has a limited effect on the surface tension, yet it significantly decreases the WRV. The effect of CTAB and SDS are indeed synergistic, confirming that there are two mechanisms which enhance the water removal process. Further, the data of Figure 4.15 suggest that water removal may potentially be improved even in systems which already have low surface tensions by the addition of CTAB. It is also noted that the order of surfactant addition is important for the synergistic effect. Presumably this fact arises due to the system favoring SDS at the air/water interface

(as evidenced by SDS decreasing surface tension more effectively than CTAB) resulting in additional CTAB adsorption on the fiber surface or presence in solution.

4.2.6. CTAB Addition with a Micro Particle Retention System

Many different wet-end chemistries are used in papermaking. In order to determine how CTAB addition would affect a commercial system, the addition of CTAB was compared with, and used in conjunction with, an industry leading retention and drainage microparticle system. BASF's Telioform system was selected upon the recommendation of several practitioners in the field (Paradis 2008). The Telioform system is comprised of BASF Percol E22S, BASF Hydrocol 2D6, BASF Alcofix 189, and BASF Telioform M306. A control system with recycled directory pulp was tested (control in Figures 4.16 and 4.17), followed by a 1 wt% addition of CTAB while pulping (CTAB). A batch of pulp was prepared and the Telioform system added under a high shear mixing environment (Telioform). The Telioform system addition was repeated with a batch of pulp previously treated with 1 wt% CTAB (CTAB w/ Telioform). Finally a pulp was prepared via addition of the Telioform system followed by the addition of 1 wt% CTAB (Telioform w/ CTAB). Figure 4.16 presents WRV data resulting from the measurements, while Figure 4.17 presents corresponding surface tension data.

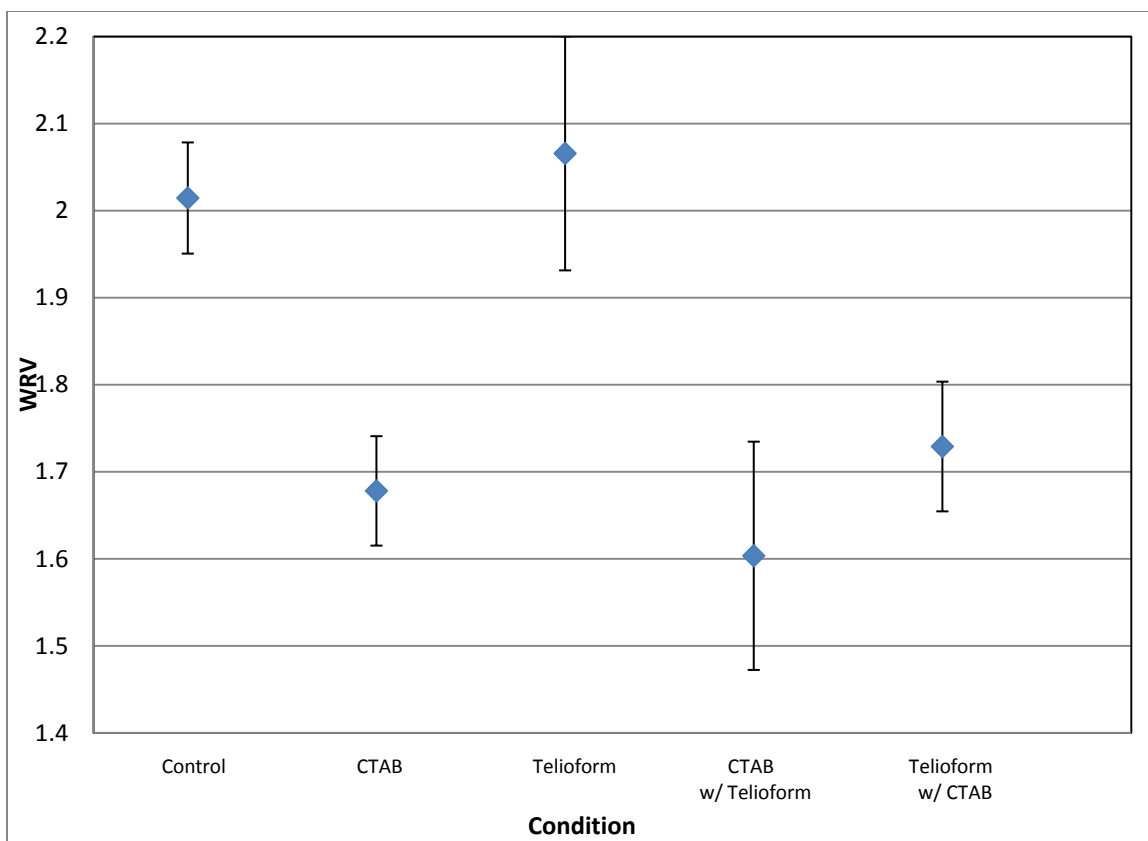


Figure 4.16. WRV comparison of 1wt% CTAB addition with the Telioform system.

It is evident from Figure 4.16 that the Telioform system on its own had no effect on the WRV; however, with the addition of CTAB prior to, or following the addition of the Telioform system, a very significant decrease in the WRV was observed. It is concluded that CTAB may be used in a synergistic manner with retention and drainage aids, or at least with the industry's leading microparticle system. That is, wet-end chemistries in paper machine systems do not necessarily need to be changed in order to obtain the water removal enhancements deriving from the addition of CTAB.

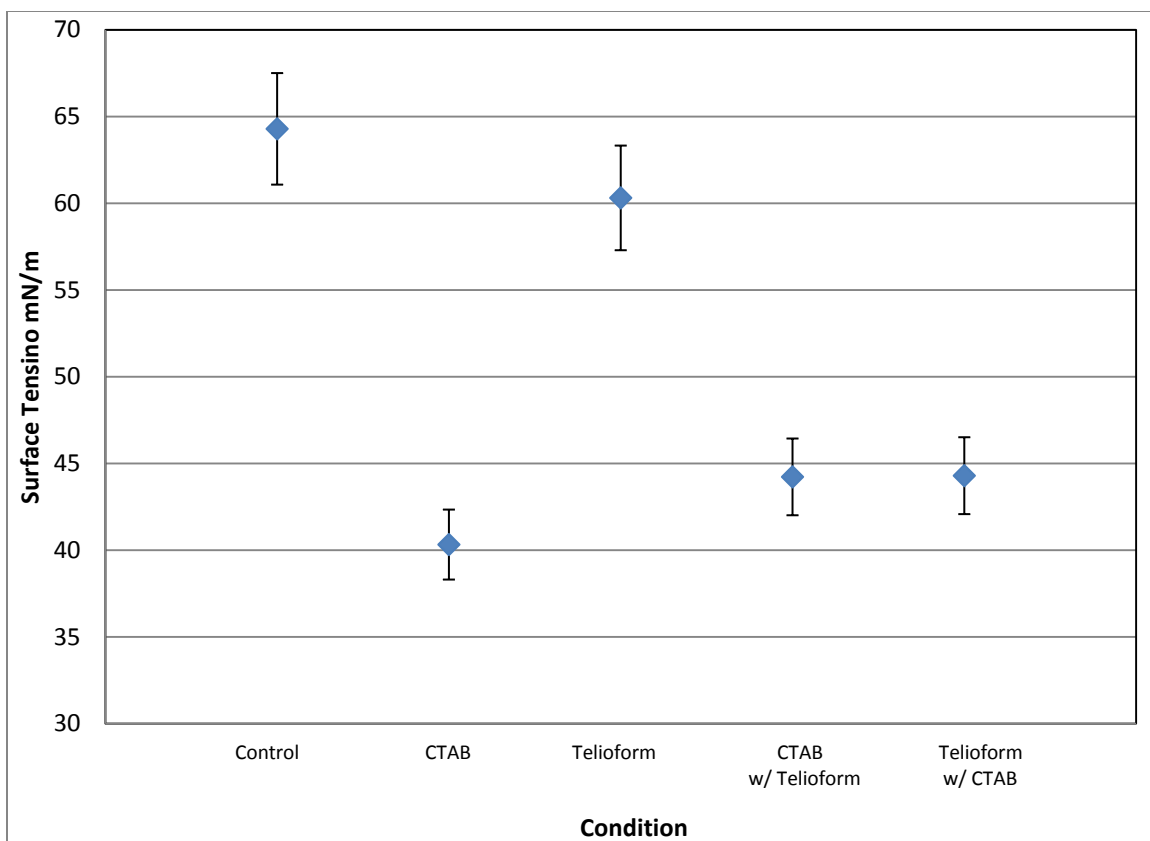


Figure 4.17. Surface tension comparison of 1wt% CTAB addition with the Telioform system.

Figure 4.17 presents surface tension data that correlates with the WRV data of Figure 4.16. It is evident from Figure 4.17 that the Telioform system on its own does not significantly affect the surface tension of the system, nor does it significantly modify the effect of CTAB on the surface tension when the two are present simultaneously.

4.2.7. Contact Angle Within Capillaries

A contact angle instrument was designed and built to image water contact angle within glass capillaries, and to measure the capillary height, see Section 3.2.2.7 for details. Through the use of complementary surface tension data, a comparison

of measured capillary forces could therefore be made with those predicted by the Young-Laplace equation in order to probe the effects of pore radius and contact angle, in addition to surface tension. Figure 4.18 presents an image of two capillaries, the left capillary is immersed in 1 mM CTAB solution, whilst the right capillary is immersed in 18.2 M Ω -cm water.

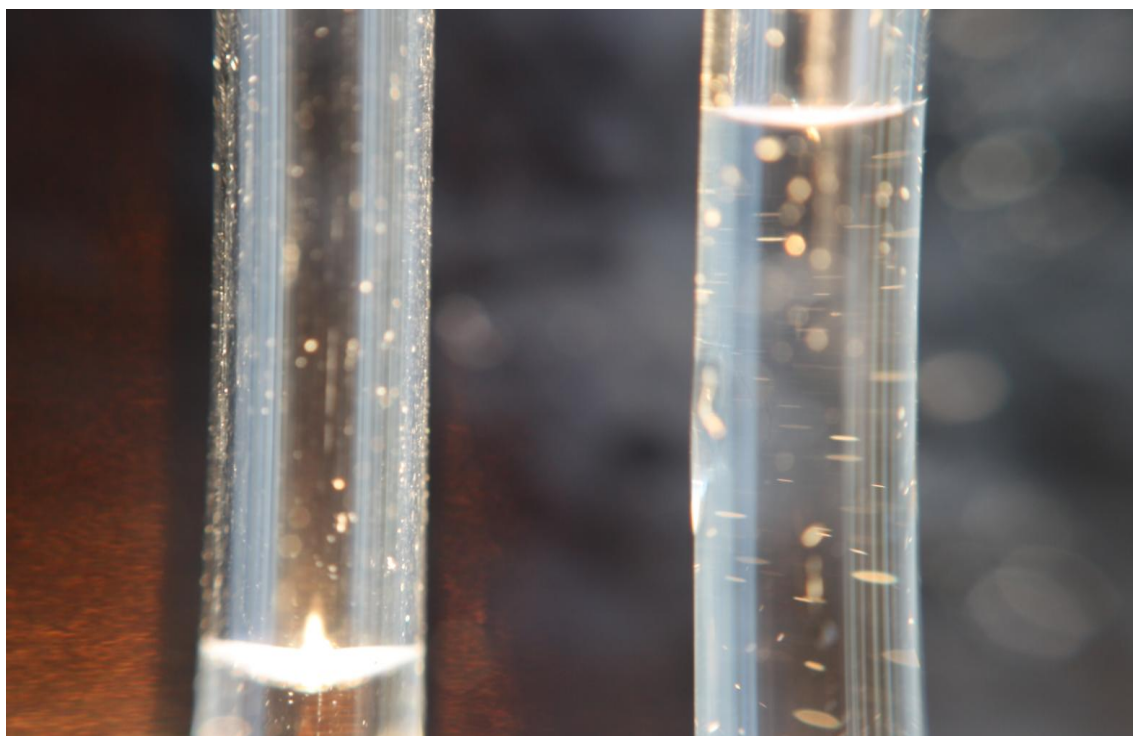


Figure 4.18. Glass capillaries with lower ends immersed in 1mM CTAB solution (left) and 18.2 M Ω -cm water (right).

It is evident from Figure 4.18 that the addition of 1 wt% CTAB decreased the capillary height relative to that of pure water (approximately 4.5 mm in the 0.75 mm diameter tube). Further, the contact angle for the CTAB solution was determined to be $\sim 55^\circ$, versus $\sim 80^\circ$ for the water control capillary. Employing the measured surface tension data, known capillary radius, and the contact angle data, the Young-Laplace equation coupled with the relationship $P = \rho gh$, results in a

predicted capillary height difference of 4.9 mm. The actual capillary height difference (4.5 mm) agrees within $\sim 10\%$; with the error largely attributable to experimental uncertainty. The accurate prediction of capillary height based upon measured surface tension and contact angle implies that the effect that CTAB exhibits in enhancing water removal is at least partially dependent upon these parameters and by inference that the pore radius should be important according to the Young-Laplace equation.

4.2.8. Surfactant Solution Concentration

Quantification of the concentration of CTAB in the solution phase of pulp slurries (that is not at the air/water interface, on the fiber surface, or within the fiber) was made through solution depletion attenuated total reflection infrared spectroscopy (ATR-IR, see Section 3.2.2.3.). The ATR-IR data revealed that at 1wt% addition of CTAB to a wide variety of pulps, less than 1% of the surfactant was present in solution. It follows therefore that greater than 99% of the surfactant was adsorbed onto or into the fiber, or was resident at the air/water interface. Since Figure 4.14 indicates that surface tension alone does not fully govern the WRV, this finding directs the search for the second mechanism of water removal to the fiber itself and to the modification of the fiber by CTAB.

4.2.9. System Charge Analysis

Given that the ATR-IR data revealed that the vast majority of CTAB added to the pulp was resident on, or within, the fiber the streaming potential and total

charge were measured to determine if the cationic surfactant had modified these parameters, the resultant data is presented in Figure 4.19.

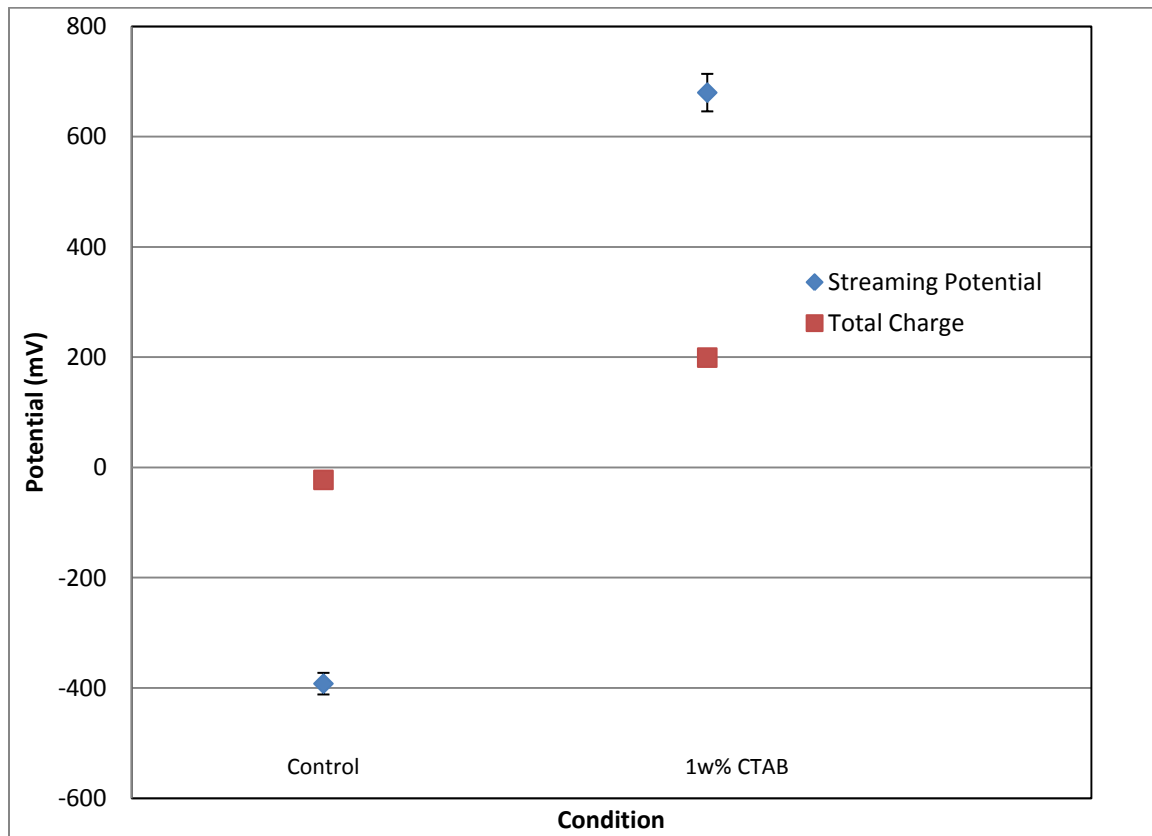


Figure 4.19. Streaming potential and total charge data for control pulp and 1wt% CTAB dosed pulp.

Figure 4.19 illustrates that when CTAB is introduced into the system, the pulp slurry undergoes charge reversal from a highly negative charge to a highly positively charged state. This finding is consistent with a large absorbed amount of CTAB which reverses the negative pulp charge by occupying anionic sites and overdosing the system.

4.2.10. Pore Radius and Bulking

The initial WRV work presented in Sections 4.2.1 and 4.2.3 provided not only data on water retention, but also yielded a dried pulp sample for examination. It was visually noted that there was a significant bulking effect upon addition of surfactants to the pulp slurry. Indeed, the addition of 1 wt% CTAB to a pulp slurry resulted in an increase in the final WRV pad thickness of greater than 50%, while the addition of SDS yielded even larger increases. Figure 4.20 presents coarse thickness measurements of WRV pads made with a variety of surfactant additives and dosages in the slurry.

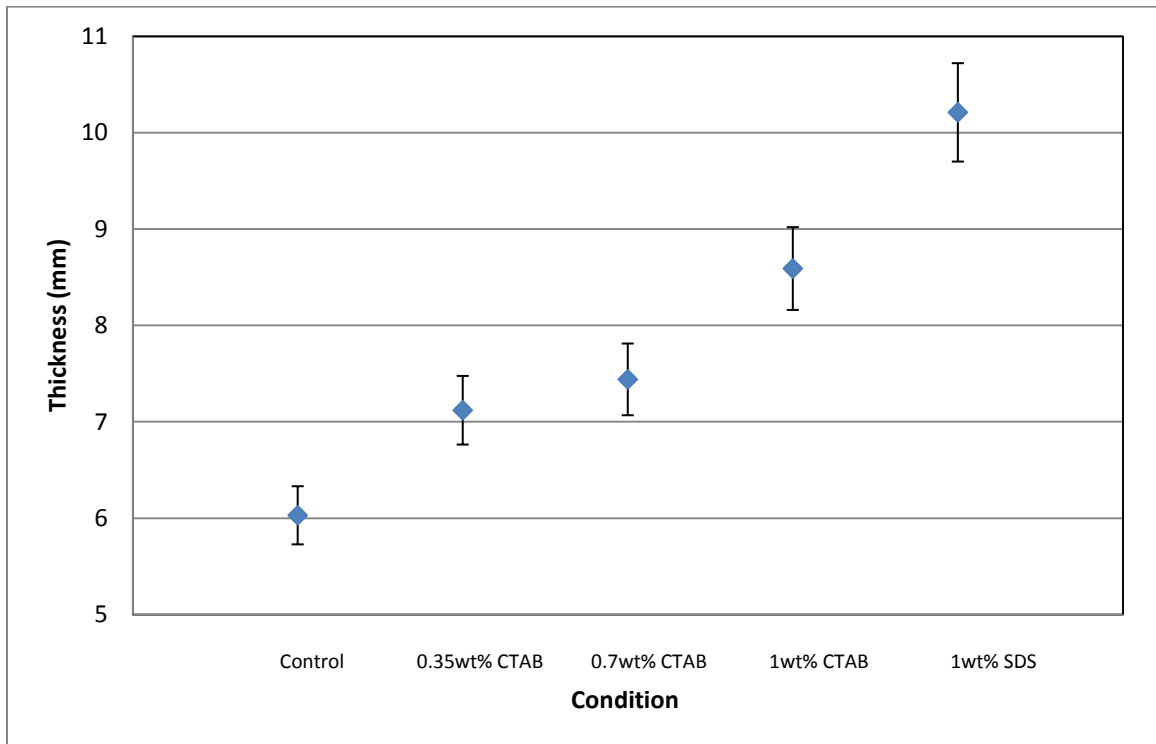


Figure 4.20. WRV pad thickness for a control, the addition of 0.35wt%, 0.7wt%, and 1wt% CTAB and 1wt% SDS.

The pad bulking evident in Figure 4.20 may potentially be due to an increase in the average pore diameter of the fiber mat, an increase in the total number of

pores, or both. The expansion was not evident in measurements of pad thickness in the wet state; yet it was clearly evident in the dried samples. This increase in the pore diameter and/or number of pores is attributed to electrostatic repulsion of the CTAB coated fibers. Specifically, if the force experience by two pulp fibers that are catatonically charged via adsorbed CTAB is modeled using Coulomb's Law, the origin of the expansion upon drying becomes evident. Coulomb's Law is defined such that q_1 and q_2 are two point charges, ϵ_0 is the relative permittivity of the bulk media, and r is the distance between them.

$$F_c = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2}$$

If one sets q_1 and q_2 as constant values and substitutes the assigned values for the permittivity of air (~ 1 F/m) and water (~ 80 F/m), it is evident that the electrostatic repulsion causing fiber separation is 80 fold in the dried state (in air) relative to the wet state (in water), resulting in a thicker dried pad.

In order to quantify the pore structure of the dried pad, mercury porosimetry was employed. Figure 4.21 presents a plot of Log Differential Volume vs. Log of Pore Diameter for WRV pads created from slurries containing various CTAB dosages during a 7 minute pulp time of recycled fiber.

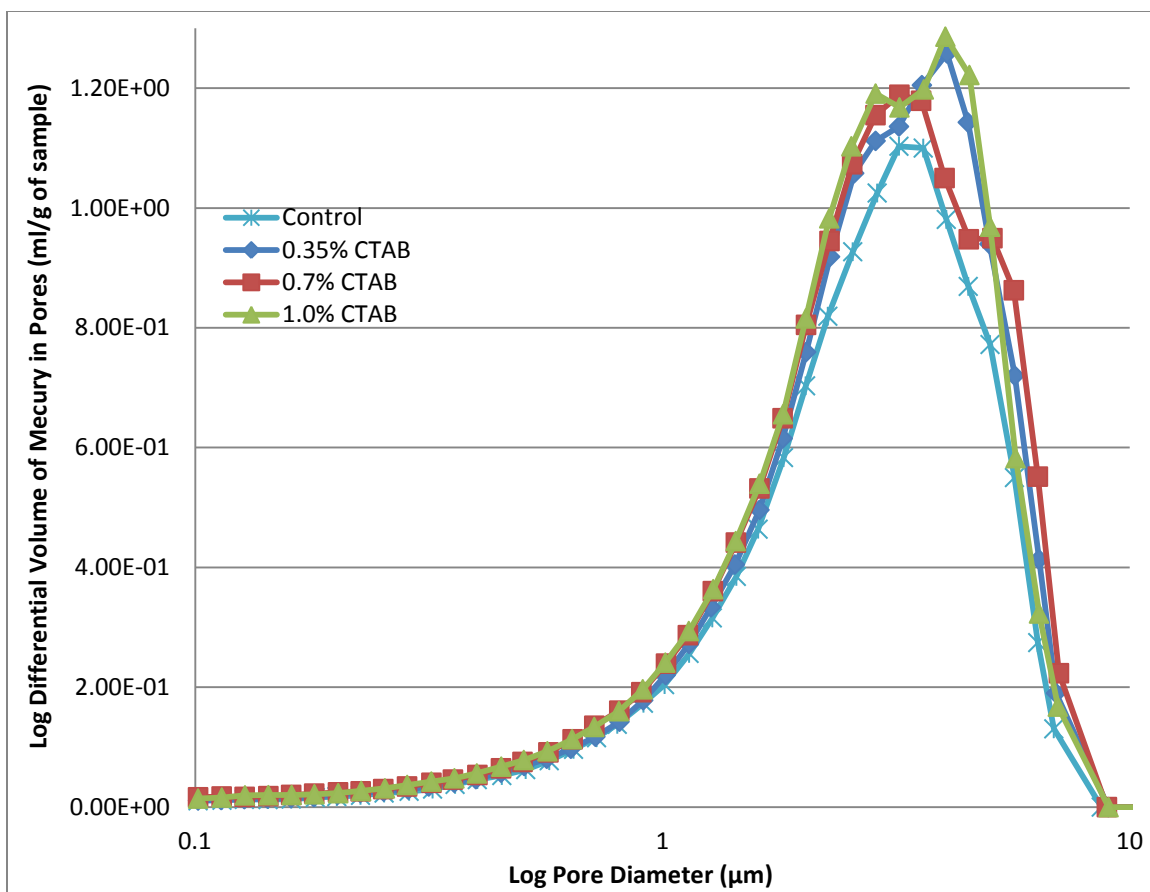


Figure 4.21. Mercury porosimetry data plotting log differential volume versus log pore diameter of WRV pads. A control condition and the addition of 0.35wt%, 0.7wt%, and 1wt% CTAB.

Figure 4.21 indicates that an increase in CTAB dosage increases the total number of pores in the resultant pad (as evidenced by the increase in total volume of pores of a given size), in addition to inducing a slight shift to larger pore sizes. The increase in both the number of pores and the shift to larger pore sizes is consistent with the observed bulking. Although only a small portion of the bulking observed in the dry state is expected in the wet state, an increase in the pore size and volume is nonetheless predicted and would be expected, according to the Young-Laplace equation, to enhance the water removal rate. It should be noted that

the bulking and the concomitant decrease in fiber-fiber hydrogen bonding may also be expected to affect sheet strength.

4.2.11. Sheet Strength

In order to examine the effect of CTAB addition on sheet strength properties, the tensile index of handsheets, made as a function of CTAB dosage, was measured.

Figure 4.22 presents the resultant the tensile data.

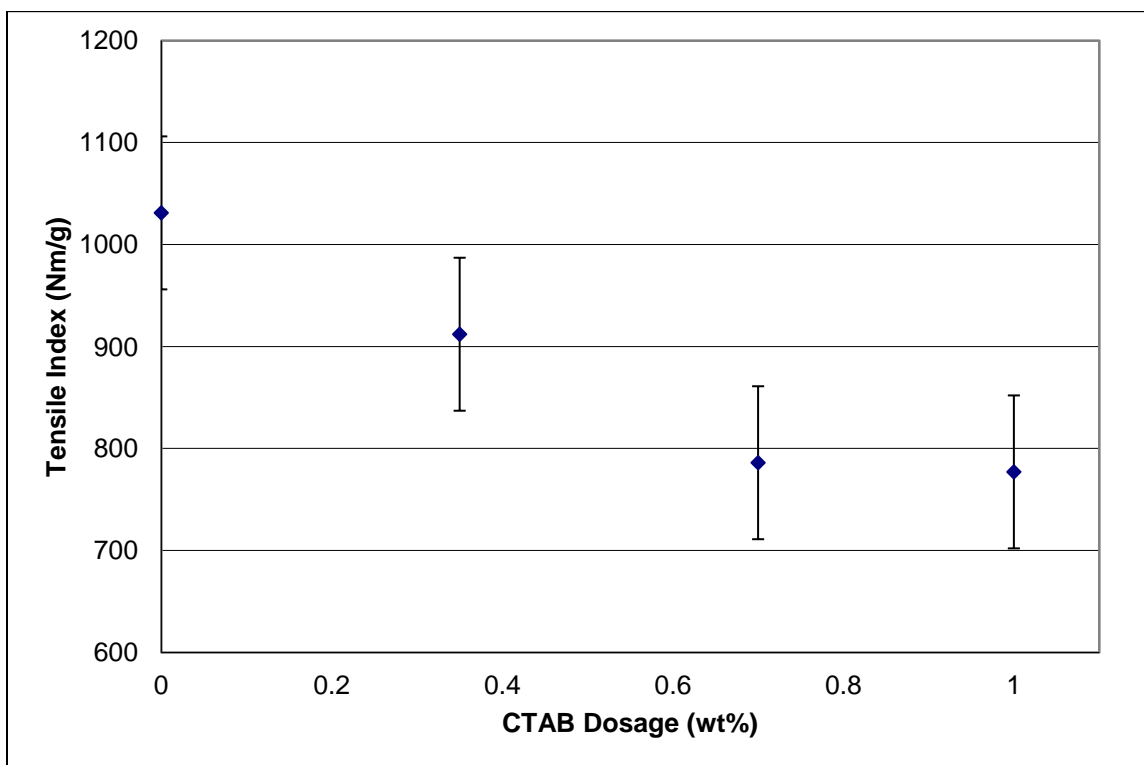


Figure 4.22. Tensile index of handsheets comprising of a control and the addition of 0.35wt%, 0.7wt%, and 1wt% CTAB.

The tensile data of Figure 4.22 suggests that there is a small, but statistically significant, decrease in sheet strength with increasing CTAB dosage. Such an effect may potentially arise from the bulking of the sheet evident in Figure 4.22 leading to decreased fiber-fiber contact and hence a decreased number of fiber-fiber hydrogen

bonds. In addition the strength loss could derive from surfactant on the fiber surface inhibiting the formation of hydrogen bonds, or potentially from a combination of the two effects. Hydroxyl number testing was employed to probe the effect of CTAB on the hydroxyl content of the fibers; the resultant data is presented in Figure 4.23.

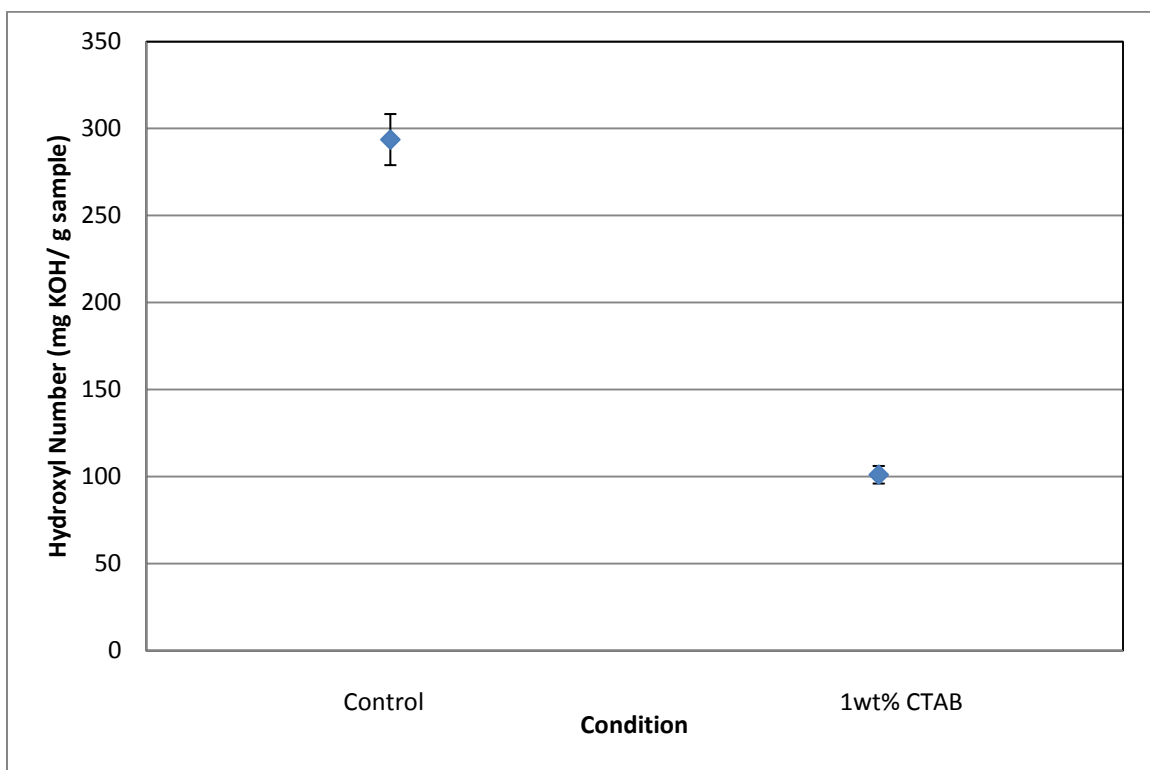


Figure 4.23. Hydroxyl number of a control condition and the addition of 1wt% CTAB.

Figure 4.23 provides evidence that the addition of CTAB to a pulp slurry results in a reduction of accessible hydroxyl groups through CTAB adsorption on or within the fibers. The control condition hydroxyl number is comparable to data presented by Tze (2001) for virgin softwood and hardwood kraft fibers of ~300. Employing the fact that each β -D-glucopyranose repeat unit of cellulose comprises 6 hydroxyl groups (Figure 1.3), it is calculated that the total number of hydroxyl

groups in the 40 grams of fiber utilized in pulp preparation is $\sim 4.46 \times 10^{23}$. At 1 wt% addition to such a pulp slurry, a total of $\sim 8.78 \times 10^{25}$ molecules of CTAB are present in the system. As such there are more than sufficient CTAB molecules to occupy all the hydroxyl groups of the fiber. In addition, "Wood Chemistry: Fundamentals and Applications" by Sjostrom (1993) states that $\sim 30\%$ of the hydroxyl groups of cellulose are inaccessible (i.e. within the wood fiber wall), which correlates with the $\sim 40\%$ of available hydroxyls of Figure 4.23 that were not occupied by CTAB. These data are consistent with a reduction in the ability of the fibers to form the extensive hydrogen bonding network necessary for sheet strength to occur.

4.2.12. Thermogravimetric Analysis

Since a portion of the mechanism appears to derive from an effect at the fiber surface, and/or within the fiber itself, it was hypothesized that the energetics of bound water removal may be affected. As such, thermogravimetric analysis (TGA) was employed to probe this possibility. Figure 4.20 presents a TGA curve of percent weight loss of a 4wt% pulp sample as a function of heating time at a temperature of 110°C for both a control pulp and a 1wt% CTAB dosed pulp. The temperature of 110°C was chosen as most industrial paper machine operate dryer sections at temperatures of 110°C to 120°C (Smook 2002).

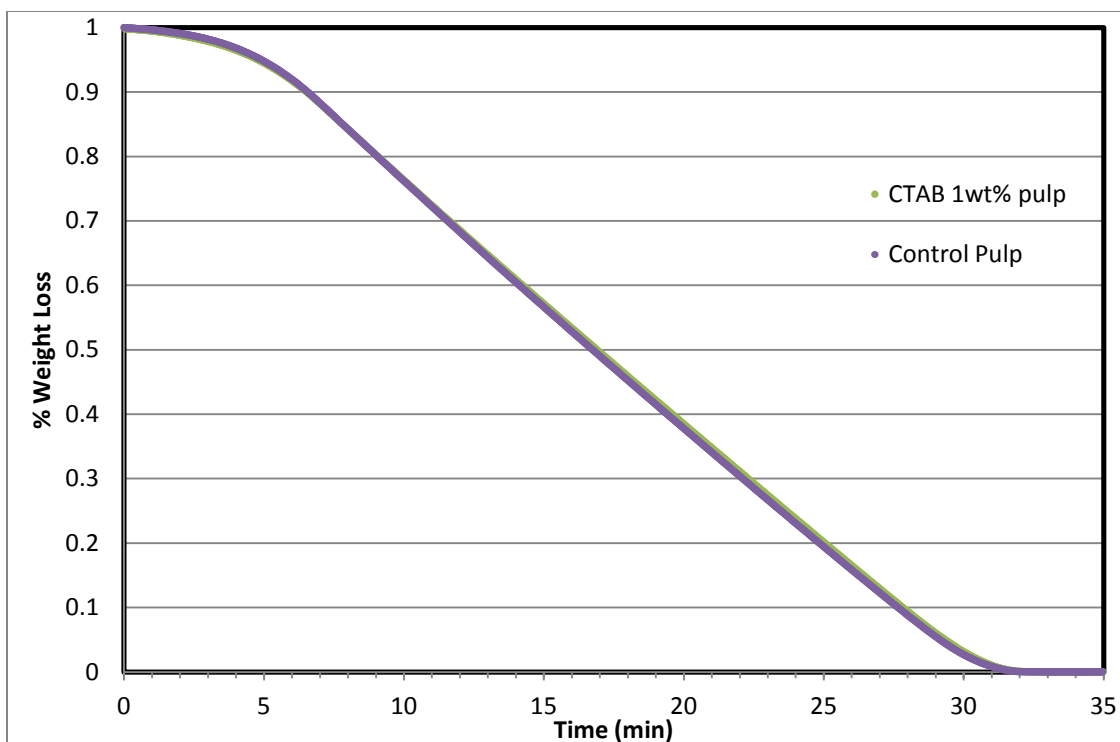


Figure 4.24. TGA trace of control pulp and 1wt% CTAB dosed pulp.

The TGA data of Figure 4.24 demonstrate that there is no change in the rate of thermal water removal from pulp fibers in the presence of 1wt% CTAB versus in its absence, suggesting that the energetics of water removal are unaffected by the addition of the surfactant. In order to determine if this laboratory result was representative of the much lower water content entering the drying section of a machine, WRV pads post centrifugation and prior to oven drying were submitted to TGA analysis. The resultant data is presented in Figure 4.25.

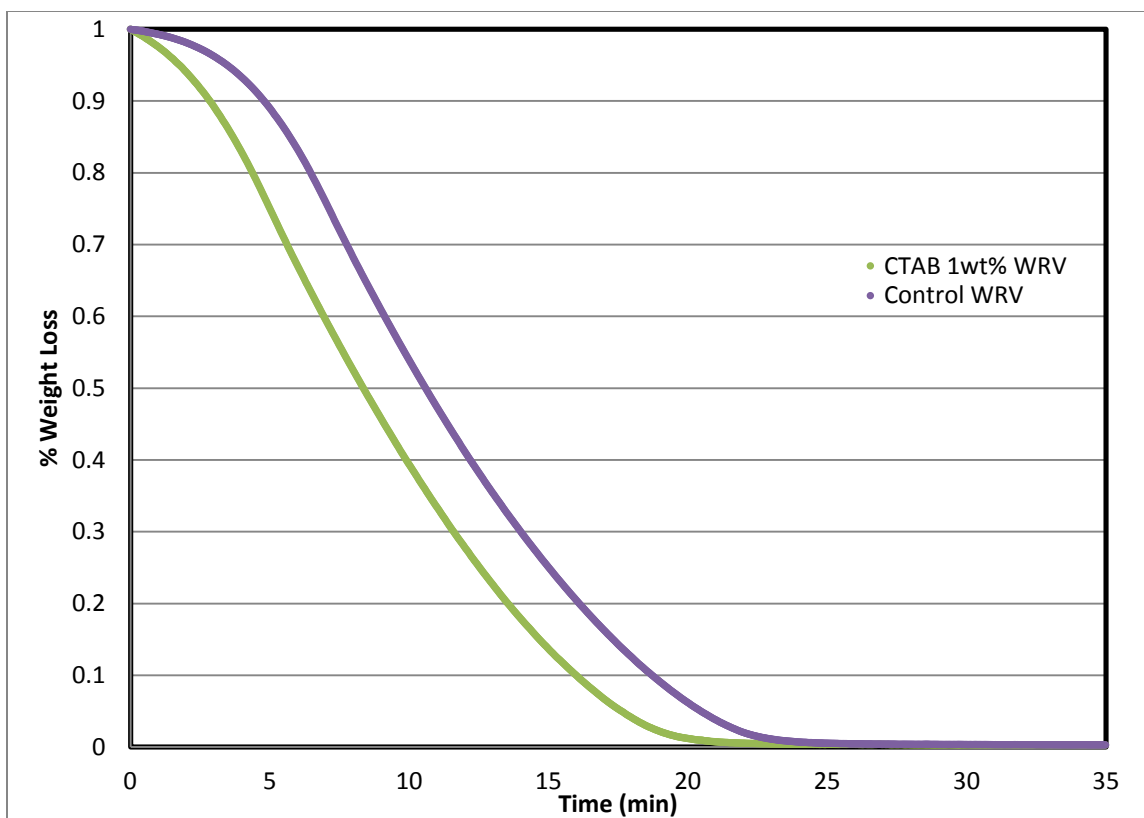


Figure 4.25. TGA trace of control WRV centrifuged pads and 1wt% CTAB dosed centrifuged pads.

Examination of Figure 4.25 reveals that although the sample modeling pulp exiting the press section dosed with 1wt% CTAB dried faster than the control pad, this is easily explained by the higher solids of the CTAB dosed pad as represented by the lower WRV values. In addition to probing the energetics of thermal water removal after the addition of CTAB, the data of Figure 4.25 provides an insight into the potential energy savings or production increases achievable by the addition of the surfactant. Specifically, the data of Figure 4.25 indicate that the CTAB treated sample dried to completion approximately 3 minutes faster than the control, correlating to a potential 15% energy reduction, or production increase. Again, no change in the slope of the constant drying regime is evident, providing additional

evidence that the mechanism by which CTAB is affecting the forming and pressing sections is not related to the energetics of water removed in the dryer section.

4.3. Conclusions

The present work has developed and characterized a novel approach to the dewatering of a cellulose fiber mat. A significant void in the literature, and subsequent opportunity, were identified; specifically, the potential to apply chemical means to enhance water removal. The data of Chapter 4 demonstrates that the addition of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, to a pulp slurry significantly decreases the amount of water retained in the pulp after drainage and pressing (examined by the water retention value test (WRV)). Drainage was progressively increased with increasing dosage of CTAB up to a plateau at a dosage level of 1wt% on a dry fiber basis. The effectiveness of CTAB was demonstrated for pulps comprising a wide range of fiber types employed in papermaking in the Northeastern United States. Employing the relationship between WRV and the solids exiting the press section of a paper machine developed by Busker (1984), the CTAB WRV results suggest a potential 4% improvement in press solids. A mass balance around a hypothetical paper machine indicates that the 4% press solids correlates with a 16% increase in production rate. In order to evaluate if the effect observed with CTAB was attributable solely to the cationic surfactant, a slew of additives were screened with WRV testing. While some additives demonstrated a performance enhancement in dewatering, none approached the effectiveness of CTAB. The screening work demonstrated that the

reduction in surface tension induced by surfactant addition was partially, but not wholly, responsible for the reduction in the WRV. Given that water removed in the forming and pressing operations is governed by flow through a porous medium (cellulose fiber mat) attention was turned to parameters affecting removal of water from capillaries. Specifically, investigation of the Young-Laplace equation led to examination of the effect of CTAB on the contact angle of water at the solid/liquid interface. Measurements within capillaries demonstrated that the addition of CTAB significantly increased the contact angle, which in turn decreased the water column height, a finding that would improve water removal in a fibrous mat. Evaluation of the solution concentration of CTAB revealed that vast majority of the surfactant was resident either at the air/water interface, or on or within the fibers. Measurement of the streaming potential and total charge of a CTAB dosed pulp slurry revealed that CTAB was adsorbed on the cellulose fiber via observation that the previously anionic fiber system was charged reversed to a cationic system.

Visual observations of WRV pads and handsheets made from CTAB dosed pulps revealed that they were significantly thicker relative to controls. An examination of the pore structure of the WRV pads was therefore undertaken. Mercury porosimetry revealed that with the addition of CTAB, the pore structure of the fiber mat shifted to larger pore radii with a concomitant increase in the number of pores. The Young-Laplace equation indicates pore radius has an inverse relationship with capillary pressure. As such, the increase in pore radii observed in the presence of CTAB results in an enhanced rate of water removal due to a reduction in the force holding water within fiber capillaries. The strength of CTAB

dosed sheets was found to be significantly decreased relative to control sheets; a fact at least partially attributable to decreased fiber-fiber hydrogen bonding arising from the bulking. In addition, determination of the number of available surface hydroxyl groups on fibers revealed that in the presence of CTAB approximately 60% of the groups were masked by the surfactant. This effect would be expected to decrease the extent of fiber-fiber hydrogen bonding, thereby contributing to the loss of sheet strength.

CHAPTER 5

IMPLEMENTATION OF CHEMICALLY ENHANCED WATER REMOVAL ON A PILOT PAPER MACHINE

5.1. Introduction

In order to determine if the laboratory observations detailed in Chapter 4 could be scaled up, a pilot trial was designed to examine the performance of the technology on the machine scale. The University of Maine's Process Development Center (PDC) has a suite of unit operations which are available for pilot testing of papermaking processes for research and development purposes. In relation to the present work, the PDC has stock preparation capabilities (fiber disintegration and pulp refining) and a pilot paper machine.

The fiber employed in the pilot trials was received in one of two forms; final product rolls (recycled directory fiber and broke), or dry lap sheets (virgin fiber). Prior to use the fiber required rehydration (in accordance with industrial practices and as replicated by the TAPPI disintegrator in the laboratory scale work of Chapter 4). A pilot scale hydro-pulper was employed to accomplish fiber rehydration resulting in a pulp slurry which was reconstituted to approximately 4wt% consistency. Once pulp slurries were prepared they were passed through a 13 inch double disc refiner operating at approximately 1100 rpm. The refining imparted 0.8 J/m of energy into the fiber slurry, resulting in fiber fibrillation in order to promote bonding and sheet strength. However, it should be noted that refining and the resultant fibrillation of fibers increases their water holding capability. The stock

prepared by rehydration and refining was stored over night in holding tanks prior to the machine trial runs.

The PDC's pilot paper machine is one of only a handful in the United States. The machine is a Fourdrinier design with a pressurized headbox, a machine slice of 15 inches and a trim width of 12 inches. The machine is capable of speeds up to 150 ft/min at the reel. The forming section has a short free drainage run followed by a low vacuum section and a high vacuum section, respectively. The press run is a felted two press design with an open draw from the couch roll. The dryer section is a steam can dryer design and features a starch press. The machine is controlled by a DSC system which replicates most modern Fourdrinier machines.

5.2. Pilot Machine Run I

A pilot machine trial was designed to examine if the laboratory results of CTAB addition (Chapter 4) would scale up. CTAB dosages of 0.35wt%, 0.7wt%, and 1wt% were employed to replicate the successful addition on the laboratory scale. Recycled directory paper was sourced for the trial as it most closely replicated the recycled fiber employed in Chapter 4. Prior to the machine run WRVs were performed to determine the anticipated press solids. Figure 5.1 presents a decreasing trend in WRV with CTAB dosage for recycled directory pulp.

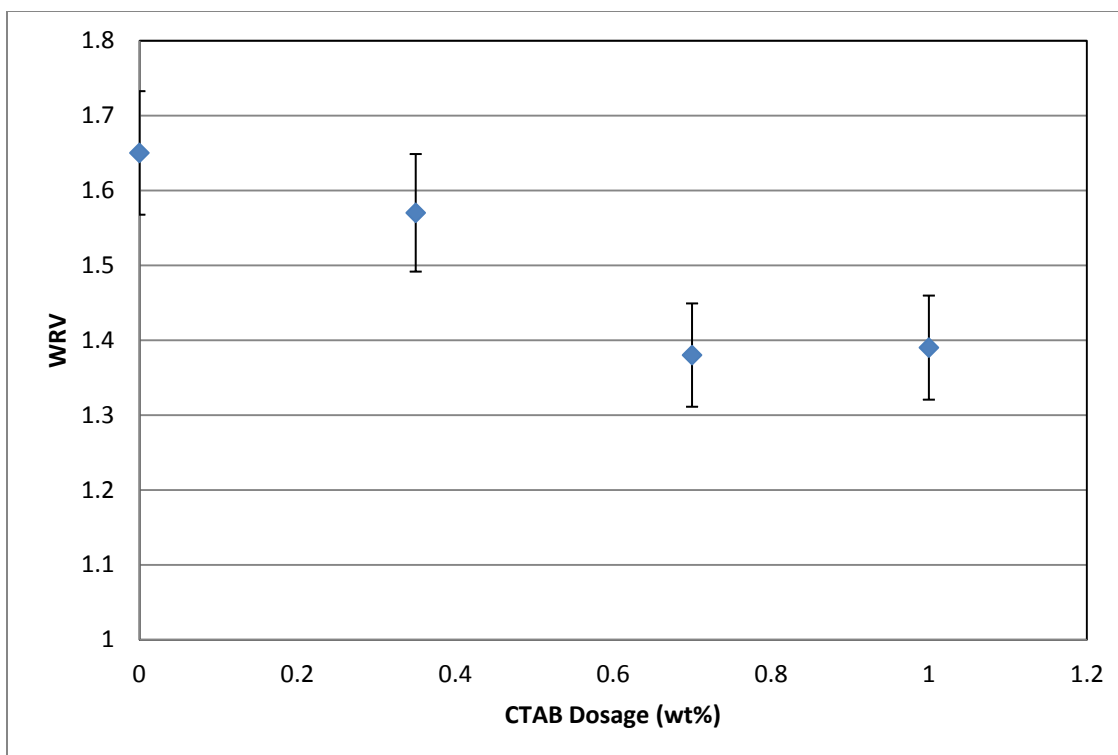


Figure 5.1. WRV of a control condition, and the addition of 0.35wt%, 0.7wt%, and 1wt% CTAB. Recycled directory fiber pulped for 7 minutes.

The trial was designed such that a control of the pulp with no chemistry was run, followed by the addition of CTAB at two separate dosages (1.0wt%, and 0.35%). These dosages provide a CTAB concentration range comparable to the laboratory work presented in Chapter 4. CTAB addition was performed by partially dissolving the surfactant in warm tap water in the mixing tank, followed by the addition of the pulp slurry to the mixing tank. The sheet specifications were set to 74 g/m² basis weight and approximately 5% sheet moisture at the reel. The recycled directory was refined to a freeness to 110 CSF. Each trial condition was run for approximately 45 minutes to ensure the machine had reached steady state prior to paper samples and representative data being collected. Pulp freeness was verified at the beginning of each trial condition. Head box samples were taken every 20 minutes for determination of pH and Mutek charge potential. A one liter head box sample was

collected at the end of each trial condition for further analysis. Paper samples were gathered after the couch, the second press, and at the machine reel to determine water content after each section of the machine as illustrated in Figure 5.2.

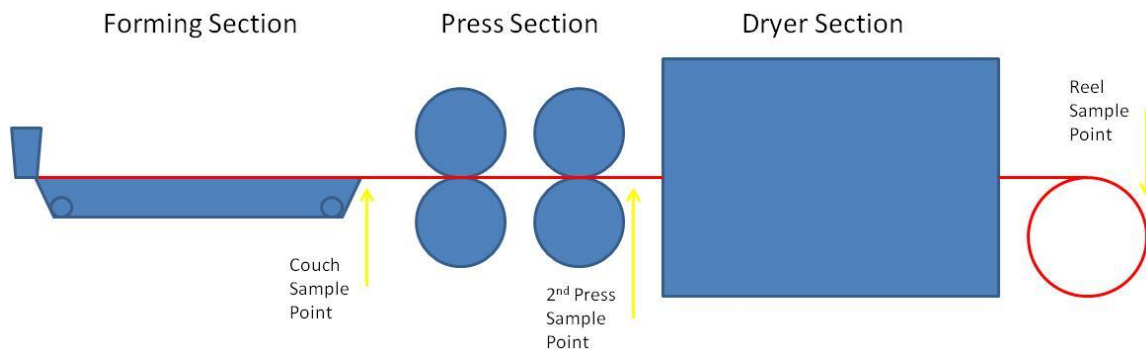


Figure 5.2. Illustration of couch, 2nd press, and reel sample points on the pilot paper machine.

A portion of each paper sample was dried on a hot plate for immediate sheet solids numbers, and three additional samples were placed in a 105°C oven overnight for final sheet solids determination. Additional paper samples from the reel were collected for sheet strength and other sheet property analysis.

Figures 5.3 – 5.5 present the measured solids as a function of CTAB dosage off the couch roll, second press, and at the reel for the recycled directory pulp.

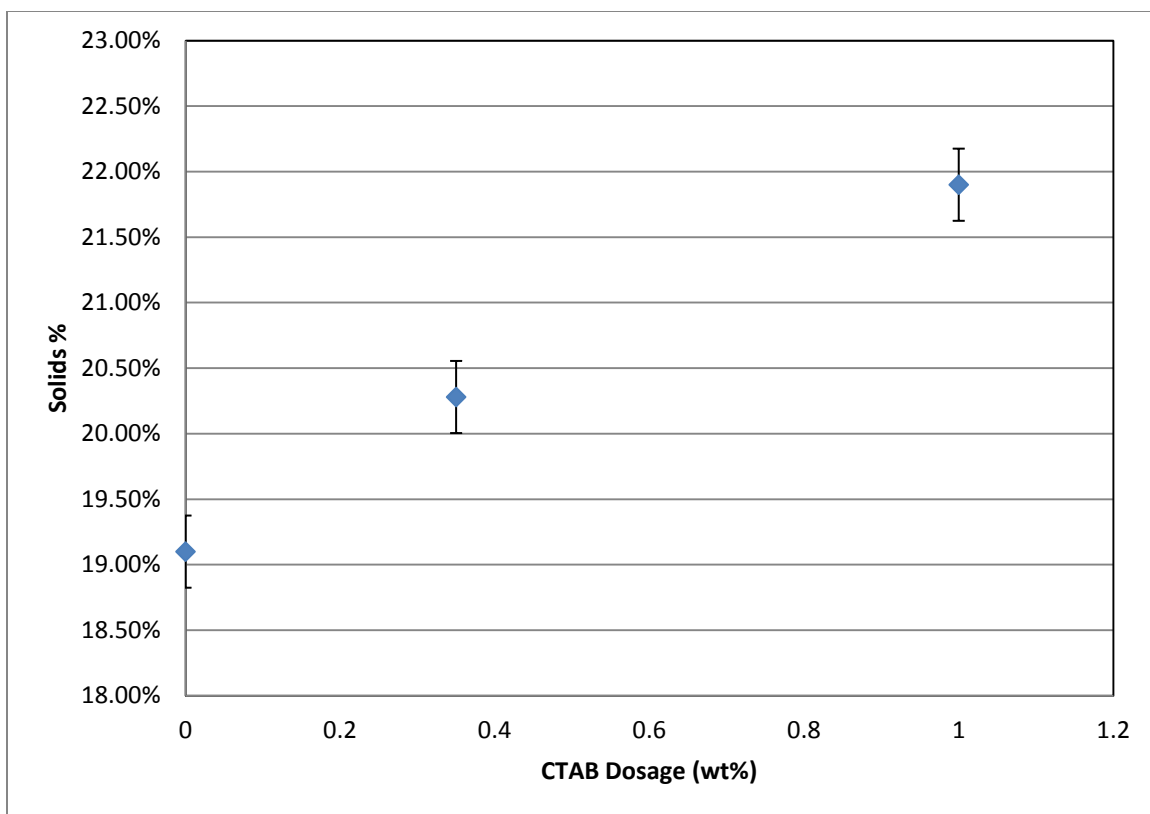


Figure 5.3. Sheet solids versus CTAB dosage off the couch roll for recycled directory pulp.

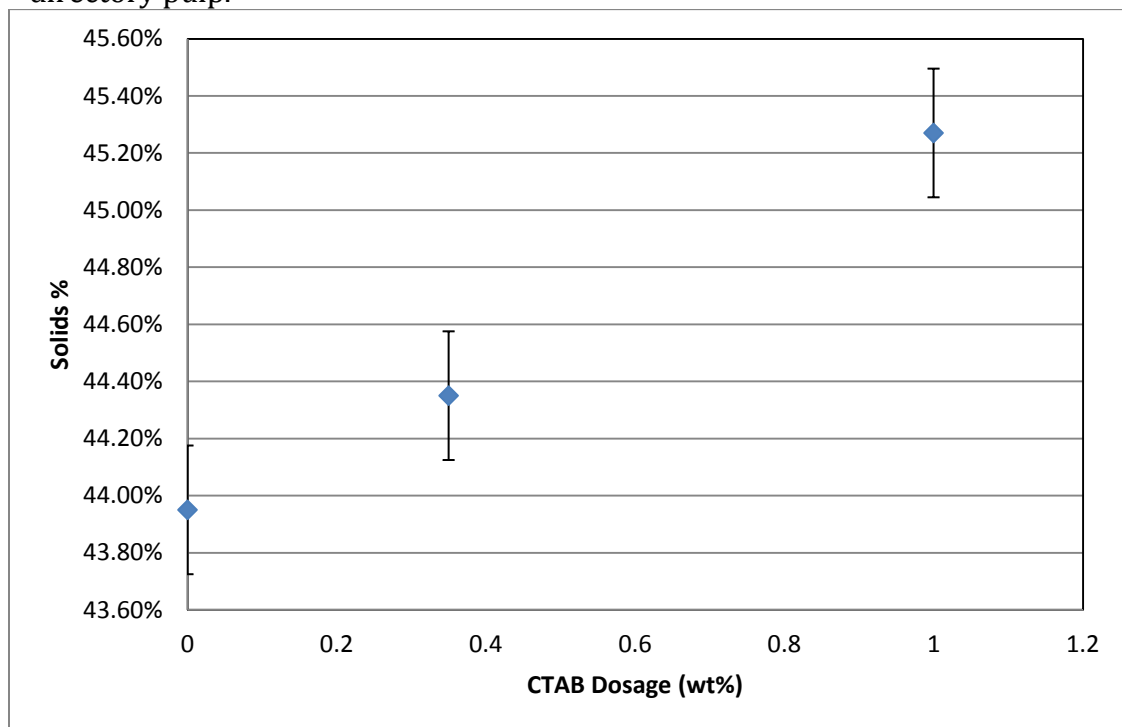


Figure 5.4. Sheet solids versus CTAB dosage off the 2nd press for recycled directory pulp.

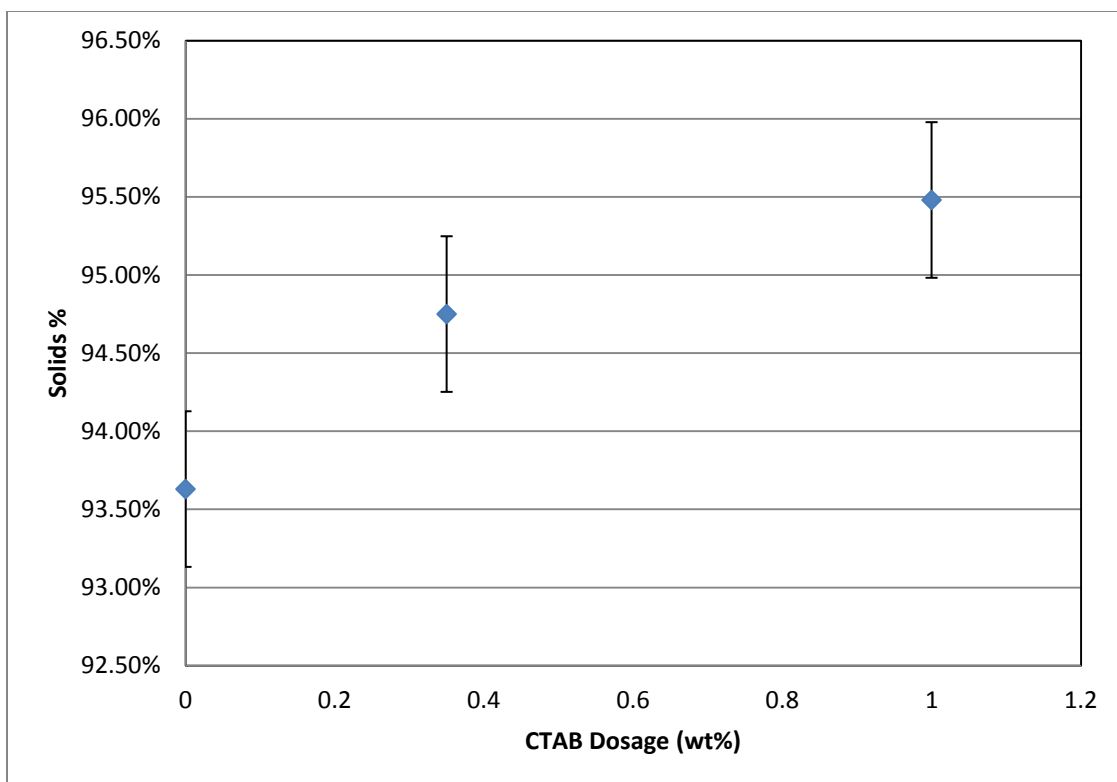


Figure 5.5. Sheet solids versus CTAB dosage off the reel for recycled directory pulp.

It is evident from examination of Figures 5.3 – 5.5 that a progressive increase in sheet solids occurred with an increase in CTAB dosage at all sample points. Indeed for the 1wt% CTAB addition condition a one and a half percent increase is displayed after the forming section, a greater than one percent increase is evident after the 2nd press, and a nearly two percent increase in reel solids is observed. It should be noted that during the trial steam pressure in the dryer section, pressing force in the press section, and the vacuum applied to the vacuum boxes in the forming section were maintained at constant values. These results are somewhat unexpected as in general an increase in couch solids does not lead to an increase in press solids or reel solids in pressing or dryer limited machines, rather the same

dryness exiting the press section is typically observed regardless of the entering solids.

Headbox charge data as a function of CTAB dosage is presented in Figure 5.6.

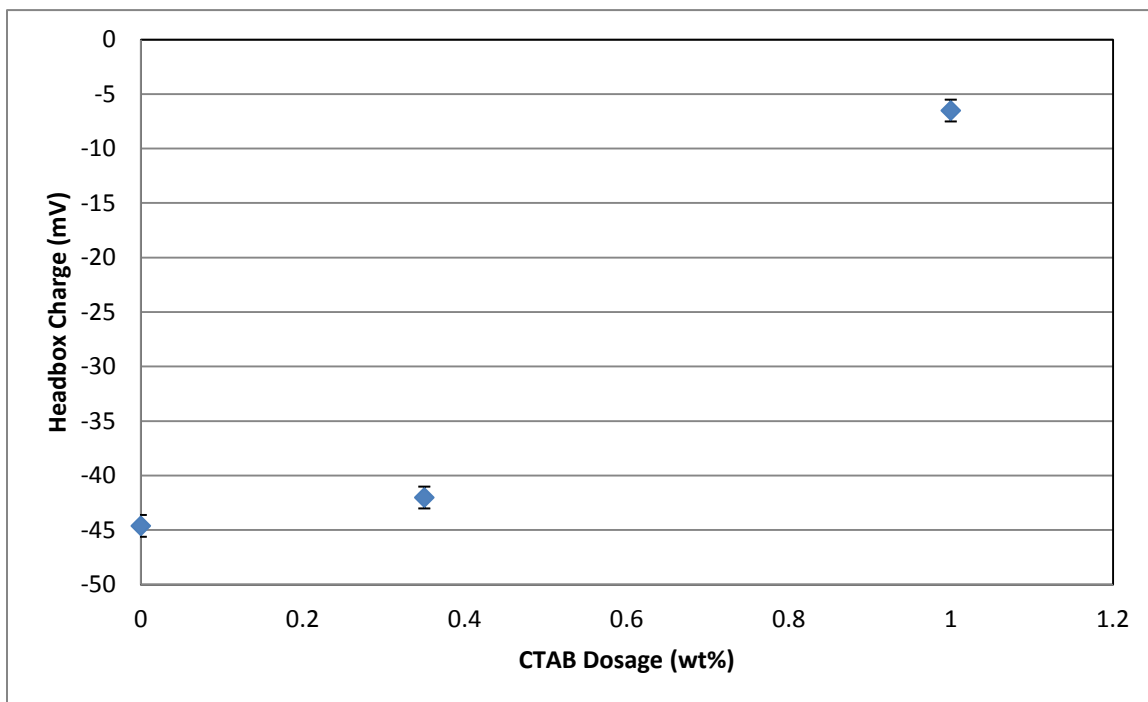


Figure 5.6. Headbox charge versus CTAB dosage for recycled directory pulp.

It is evident from Figure 5.6 that headbox charge varied progressively from a control value of -45 mV, to -42 mV at 0.3 wt% CTAB, to -7 mV at 1 wt% CTAB addition. These results are not surprising given the addition of the cationic surfactant to the system and suggest adsorption of CTAB at the solid/liquid interface of the pulp slurry. Surface tension analysis of headbox samples for each condition resulted in the data presented in Figure 5.7. As may be expected from the data of Figure 4.14, the surface tension displayed a progressively decreasing trend with the increase in CTAB dosage, corresponding with an increase in surfactant concentration at the liquid/air interface.

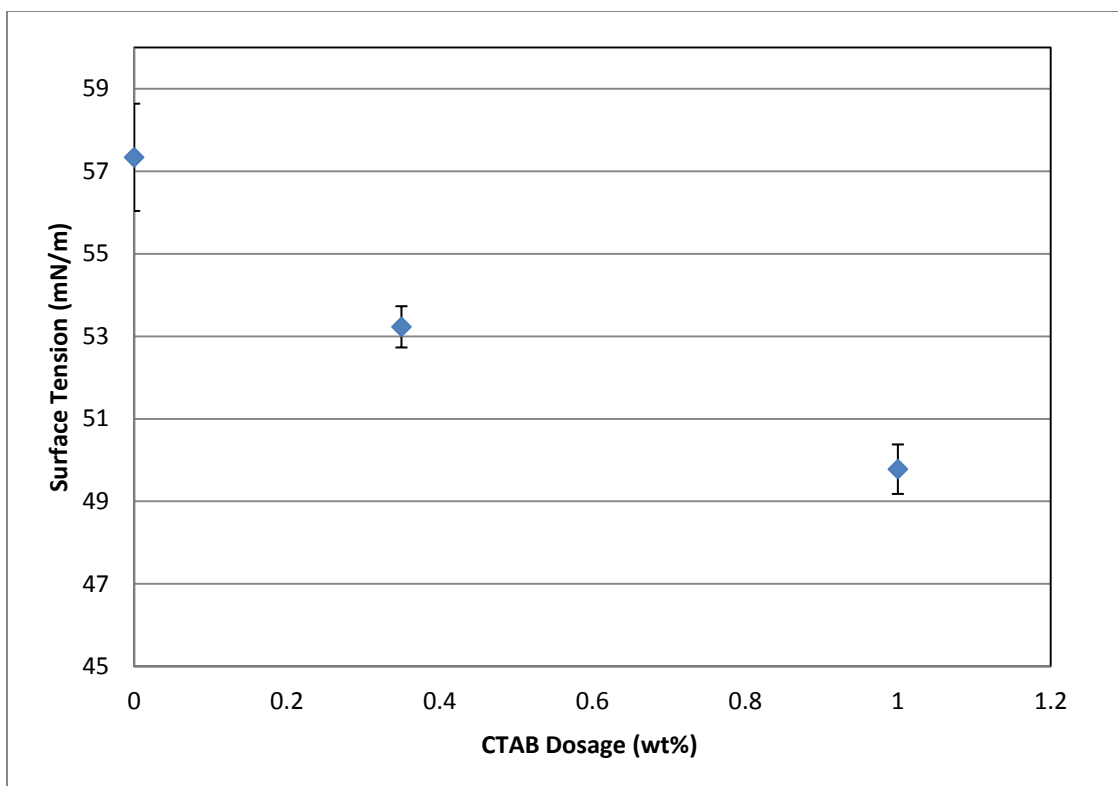


Figure 5.7. Surface tension versus CTAB dosage of headbox samples for recycled directory pulp.

The physical properties of resultant sheets were examined to determine if the trends observed in the laboratory scale data translated to the pilot scale. Specifically, sheet strength in the manner of tensile and burst was measured. In addition, sheet thickness, and pore volume and distribution were examined.

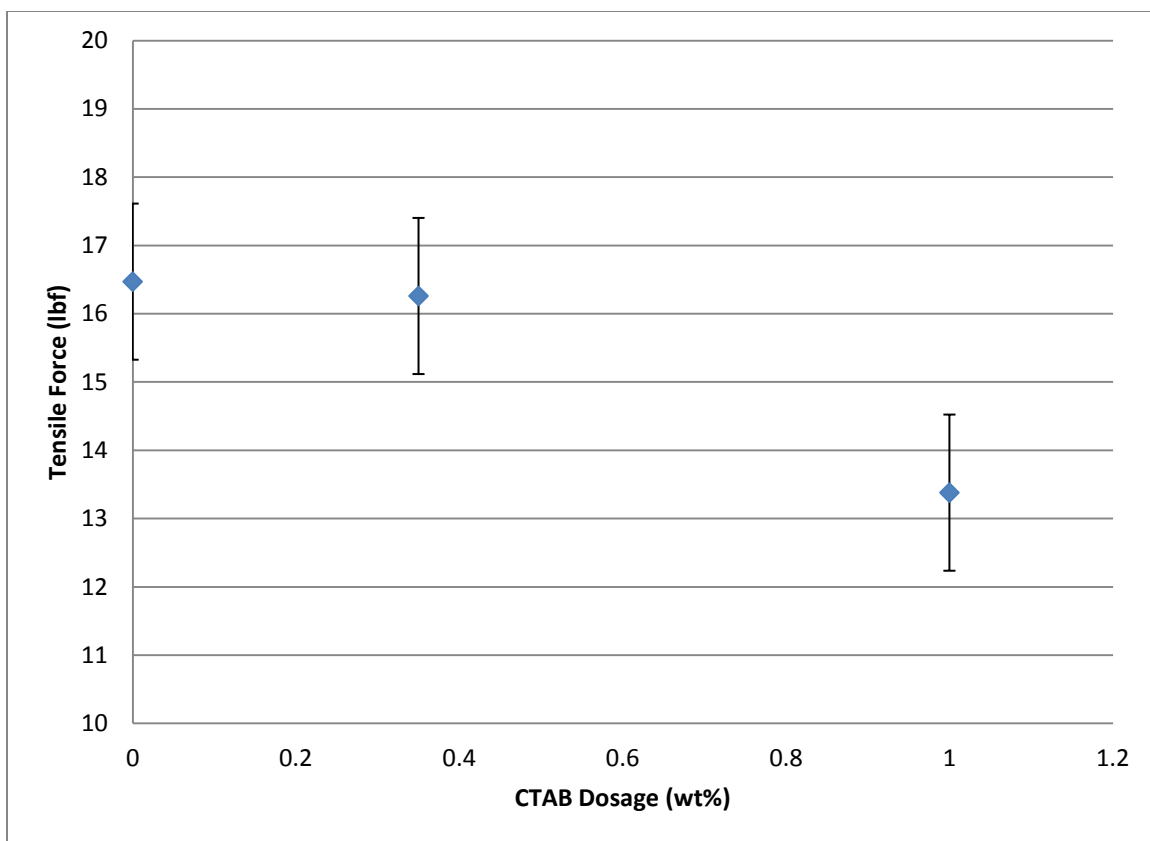


Figure 5.8. Sheet tensile versus CTAB dosage for recycled directory pulp.

Figure 5.8 presents a decrease in tensile strength of sheets as a function of increased CTAB addition. Specifically, the data demonstrates that the sheet lost nearly three lbf of strength at the highest dosage of CTAB (1 wt%). Consequently, the sheet burst strength was examined, the results of which are presented in Figure 5.9. A comparable trend to that observed for sheet tensile is evident in the sheet burst strength data.

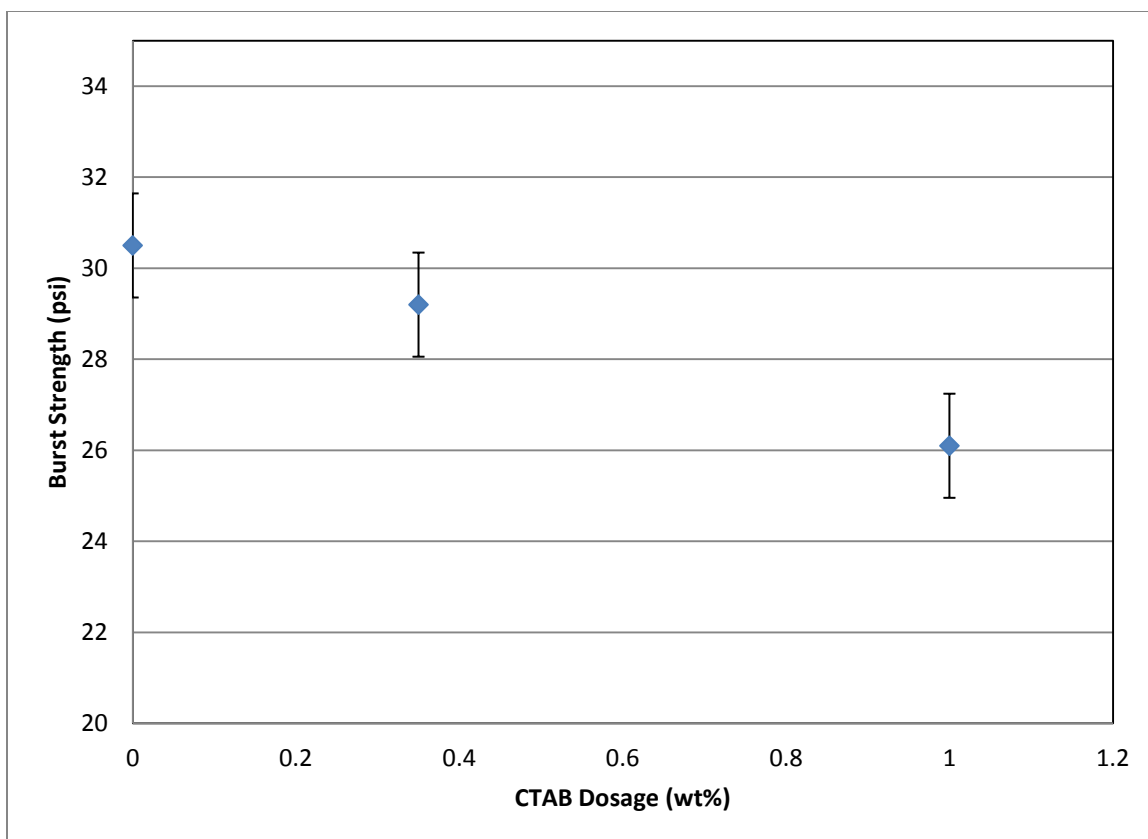


Figure 5.9. Sheet burst versus CTAB dosage for recycled directory pulp.

Throughout the pilot trial, the sheet maintained a consistent basis weight independent of CTAB dosage. However, given the sheet bulking presented in Chapter 4, the caliper of the sheets was measured. Indeed, Figure 5.10 reveals that as CTAB dosage increased, sheet thickness increased from ~5.4 mils (~137 μm) to ~6.1 mils (155 μm) at 1wt% CTAB addition, a similar trend to the laboratory data for WRV pad thickness presented in Figure 4.22.

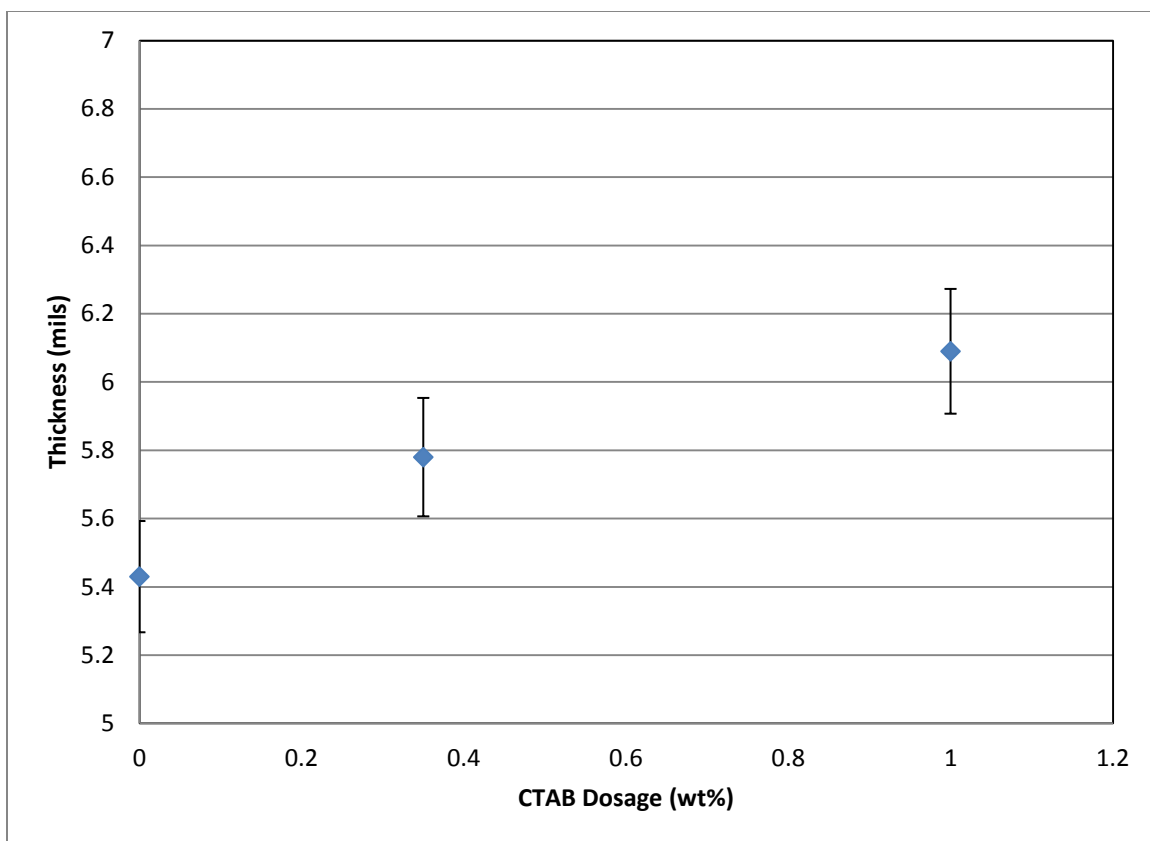


Figure 5.10. Sheet caliper versus CTAB dosage for recycled directory pulp.

The sheet bulking evident in Figure 5.10 was presumably a result of changes in the pore structure of the sheet (previously observed for WRV pads in Section 4.2.11). Consequently trial sheets were examined by mercury porosimetry, the resultant data is presented in Figure 5.11. It is evident from examination of Figure 5.11 that an increase in the cumulative pore volume of the sheets occurs with an increase in the CTAB dosage, a trend consistent with the findings of Section 4.2.11.

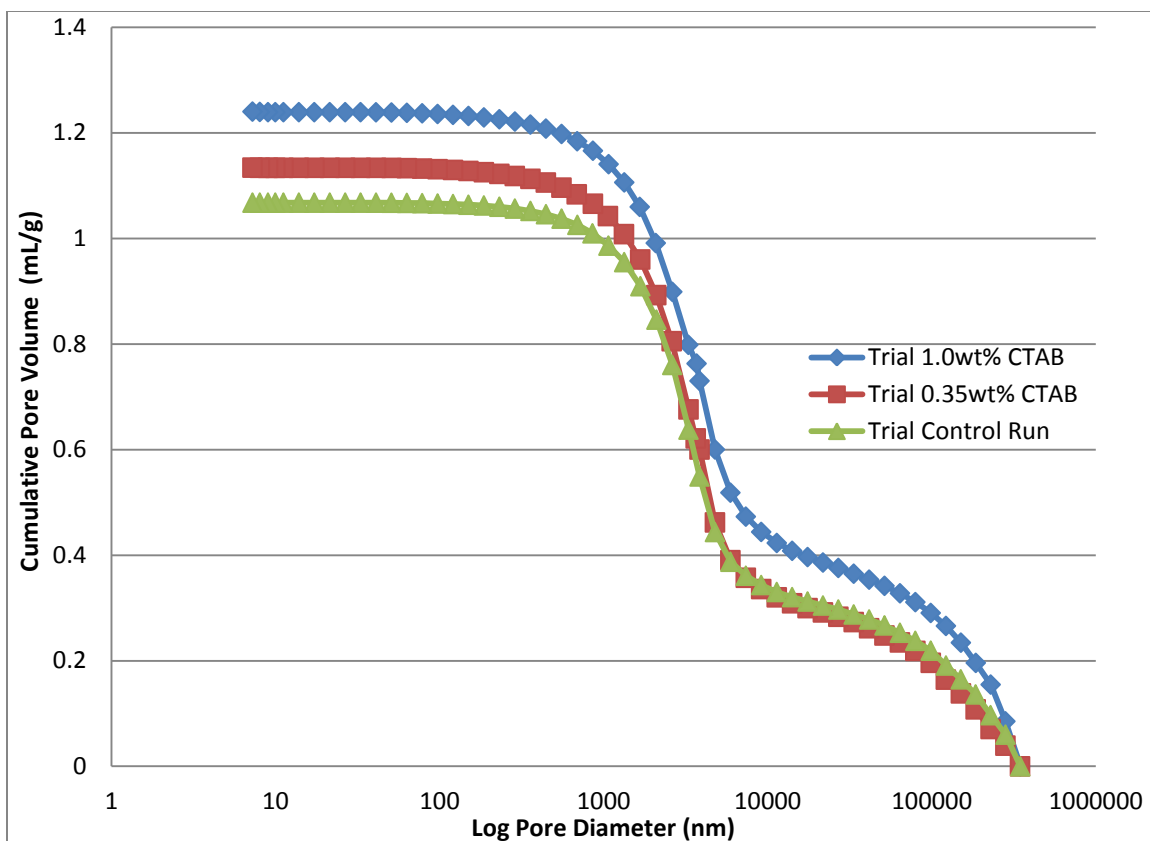


Figure 5.12. Sheet cumulative pore volume versus CTAB dosage for recycled directory pulp.

The trial results demonstrate on the pilot scale that the addition of CTAB to a pulp slurry enhances water removal in the paper making process. Indeed all trends observed from the laboratory study (Chapter 4) were successfully scaled to the pilot machine. Enhanced water removal was demonstrated in both forming and pressing sections, the headbox charge was decreased, as was bond strength of the sheet. In addition, the bulking and change in pore structure observed on the bench scale were replicated on the pilot scale.

5.3. Pilot Machine Run II

A second pilot scale machine trial was designed and implemented to examine two separate aspects of chemically enhanced water removal, scale up of the dual

addition of CTAB and the Telioform system; and optimization of the addition points of CTAB when used as the sole additive. The two day trial was structured such that the scale up feasibility of CTAB and Telioform co-addition was performed the first day, and examination of the effect of CTAB addition point was performed the second day. Critically, the trial was configured to document enhanced dewatering through quantification of production rate increases by running the machine in a dryer limited state and manipulating speed whilst maintaining reel solids of ~95%. If enhanced dewatering occurred in the forming and/or pressing section, the water load into the dryer section would decrease and machine speed could be increased to reinstate a dryer limited scenario. Such an eventuality would result in an increase in production. As such, machine speed/production was employed to quantify the effect of enhanced dewatering.

The sheet specifications were set to 89 g/m² basis weight and approximately 5% sheet moisture at the reel. Pulp was refined to ~300 CSF and the freeness was verified at the beginning of each trial condition. Head box samples were taken every 20 minutes for the determination of pH and Mutek streaming potential and total charge. Additional head box samples were acquired at each solids sample point to provide a correlated wet end sample for future testing. A one liter head box sample was collected at the end of each trial condition for further laboratory analysis. Paper samples were gathered after the couch, the second press, and at the machine reel to determine water content at each section of the machine. A portion of each paper sample was dried on a hot plate for immediate sheet solids numbers, and three additional samples were collected and placed overnight in a 105°C oven for

final sheet solids content. Additional samples from the reel were acquired to determine sheet strength and perform other sheet property analysis.

The furnish for the Telioform/CTAB slurry was comprised of 70% Sappi Co-Pulp and 30% Twin Rivers Paper single side coated broke. The broke was included in order to provide ash content to the sheet and better represent a commercial furnish. In addition, the presence of ash in the sheet allowed the monitoring of the retention efficiency of the Telioform system (drainage, forming, and retention aid). Figures 5.12 – 5.14 present sheet solids as a function of trial conditions off the couch, the 2nd press, and at the reel, respectively. The four conditions were a control with no added chemistries, Telioform only addition, CTAB addition followed by Telioform addition, and a CTAB addition only. CTAB addition was performed by introducing the additive in the machine chest. The machine speeds at each condition were as follows; control and CTAB only, 50 ft/min, and both Telioform and Telioform/CTAB, 45 ft/min. When the Telioform system was employed machine speeds had to be decreased in order to maintain the target sheet moisture at the reel.

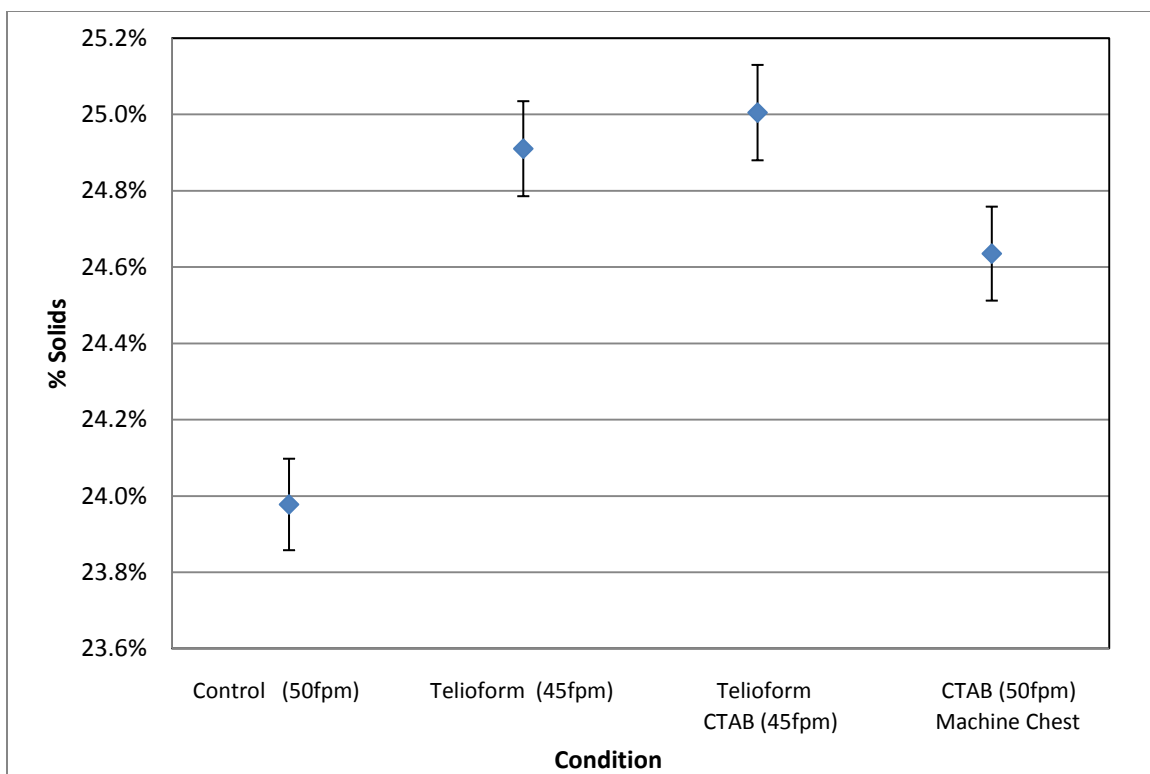


Figure 5.12. Sheet solids off the couch roll. Control, Telioform, Telioform/CTAB, and CTAB trial conditions.

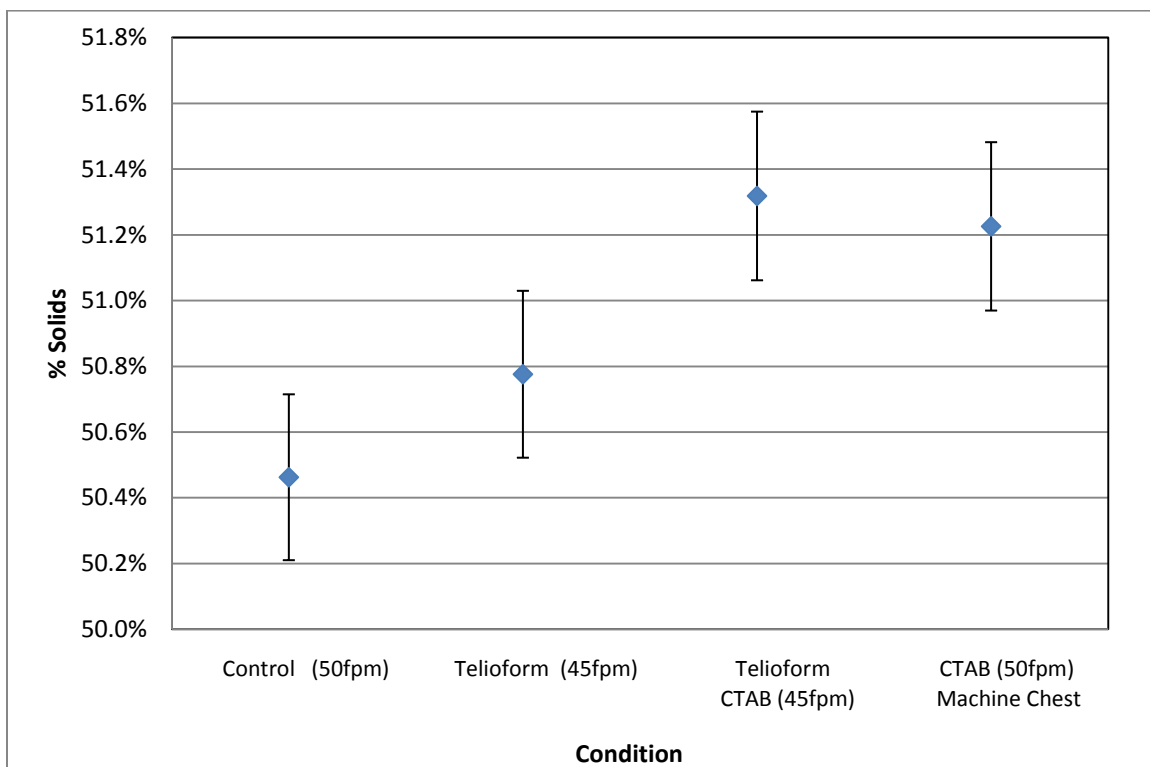


Figure 5.13. Sheet solids off the 2nd press. Control, Telioform, Telioform/CTAB, and CTAB trial conditions.

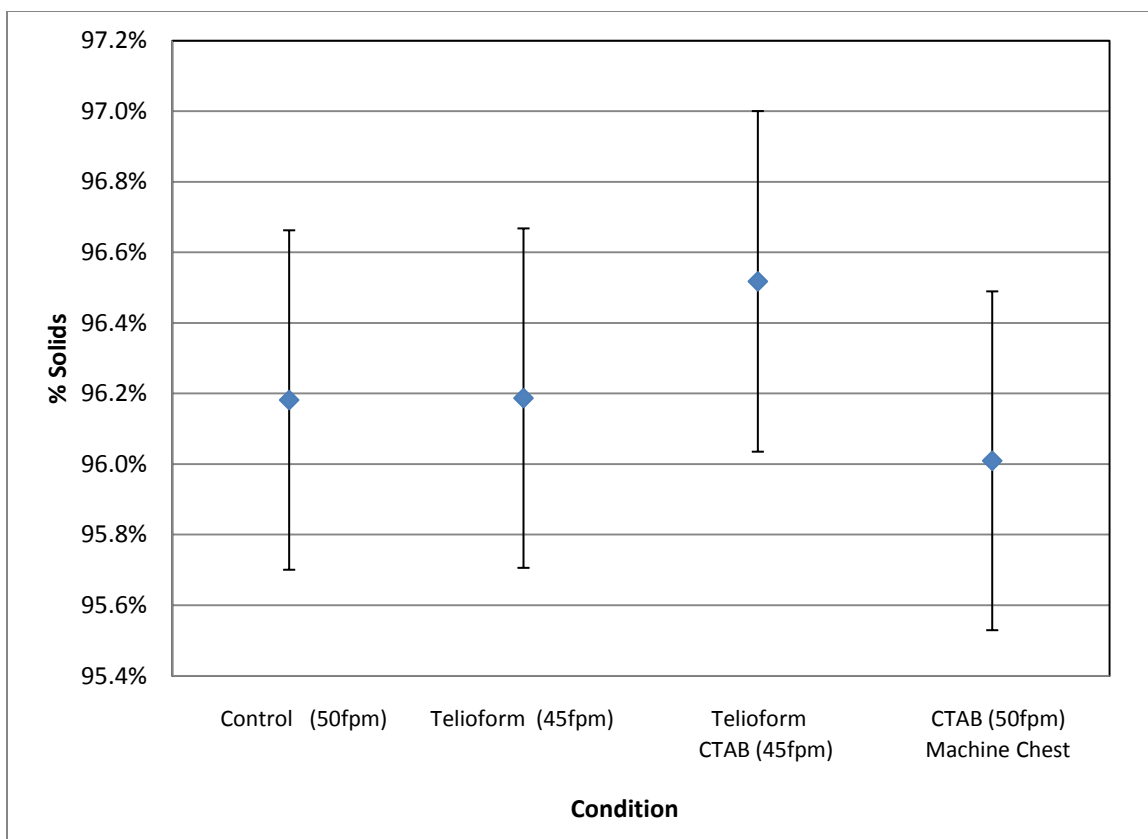


Figure 5.14. Sheet solids off the reel. Control, Telioform, Telioform/CTAB, and CTAB trial conditions.

It is evident from Figure 5.12 that for trial conditions of Telioform and Telioform/CTAB, greater water retention in the sheet occurred in the forming and pressing sections versus the control, as is indicated by the need to decrease machine speed by 5 fpm to maintain reel solids. It is noted that this finding is contrary to results seen in WRV testing presented in Figure 4.16 and is likely attributable to the fact that addition of retention chemistry to the machine furnish increases the retention of fines in the forming sheet resulting in greater water retention. The laboratory scale results presented in Figure 4.16 were performed on recycled fibers and did not include a coated broke component.

In order to verify that the origin of the greater water retention observed in the Telioform condition was due to enhanced fines retention, tray solids were monitored and are presented in Figure 5.15.

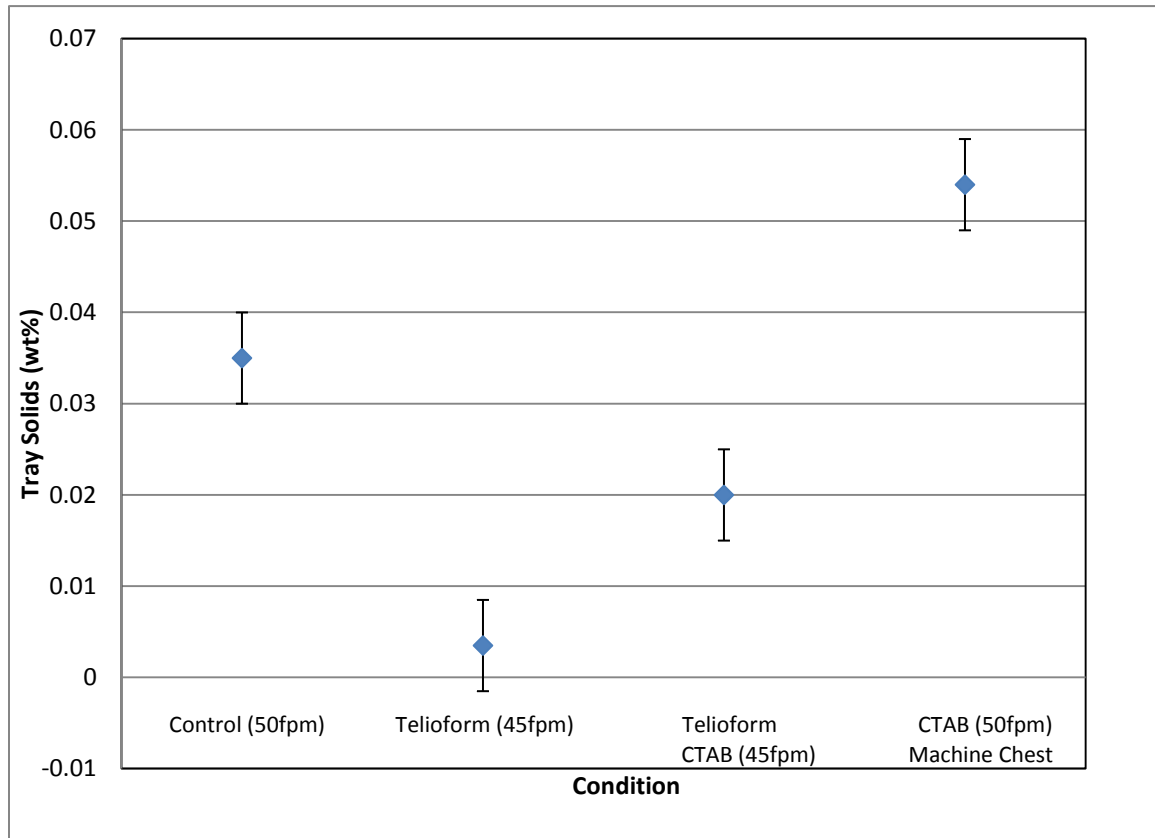


Figure 5.15. Tray solids for control, Telioform, Telioform/CTAB, and CTAB trial conditions.

Investigation of Figure 5.15 reveals a significant decrease in tray solids upon the addition of the Telioform system, verifying an increase in the amount of fines retained, correlating with a wetter sheet.

The study probing the effect of CTAB addition point on the efficiency of water removal was performed on day two of the pilot machine trial. The furnish employed for day one of the trial was employed to enable direct comparison of results. CTAB addition was performed at two distinctly different points in the furnish preparation

process to provide a large range in the residence time of the surfactant with the fiber. Specifically, in trial condition one CTAB was added prior to pulp refining, whilst in trial condition two CTAB was introduced into the disintegration water prior to addition of the pulp. The addition points utilized in the second pilot trial are illustrated in Figure 5.16.

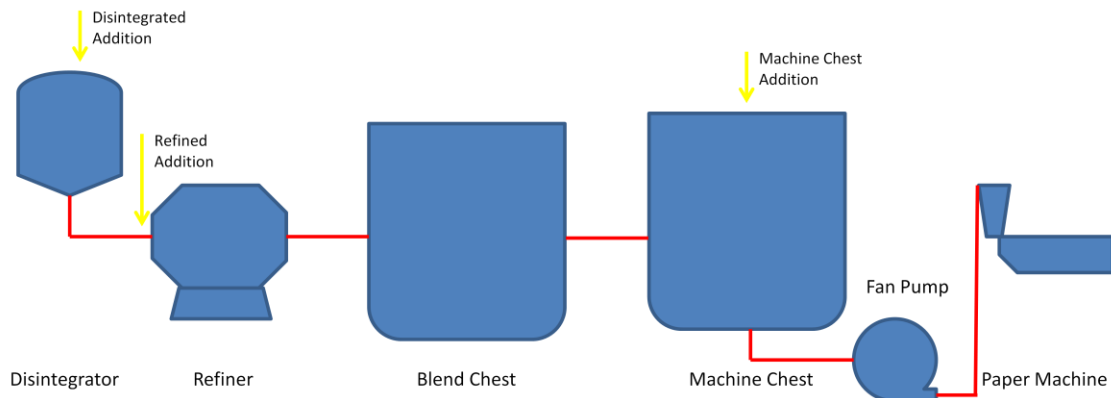


Figure 5.16. Schematic of CTAB addition points for machine chest, refined, and disintegrated trial conditions.

The optimized machine speeds for each condition were as follows; control condition, 50 ft/min, CTAB refined, 54 ft/min, and CTAB disintegrated, 59 ft/min. Figures 5.17 - 5.19 present the sheet solids at the couch, press, and reel, respectively.

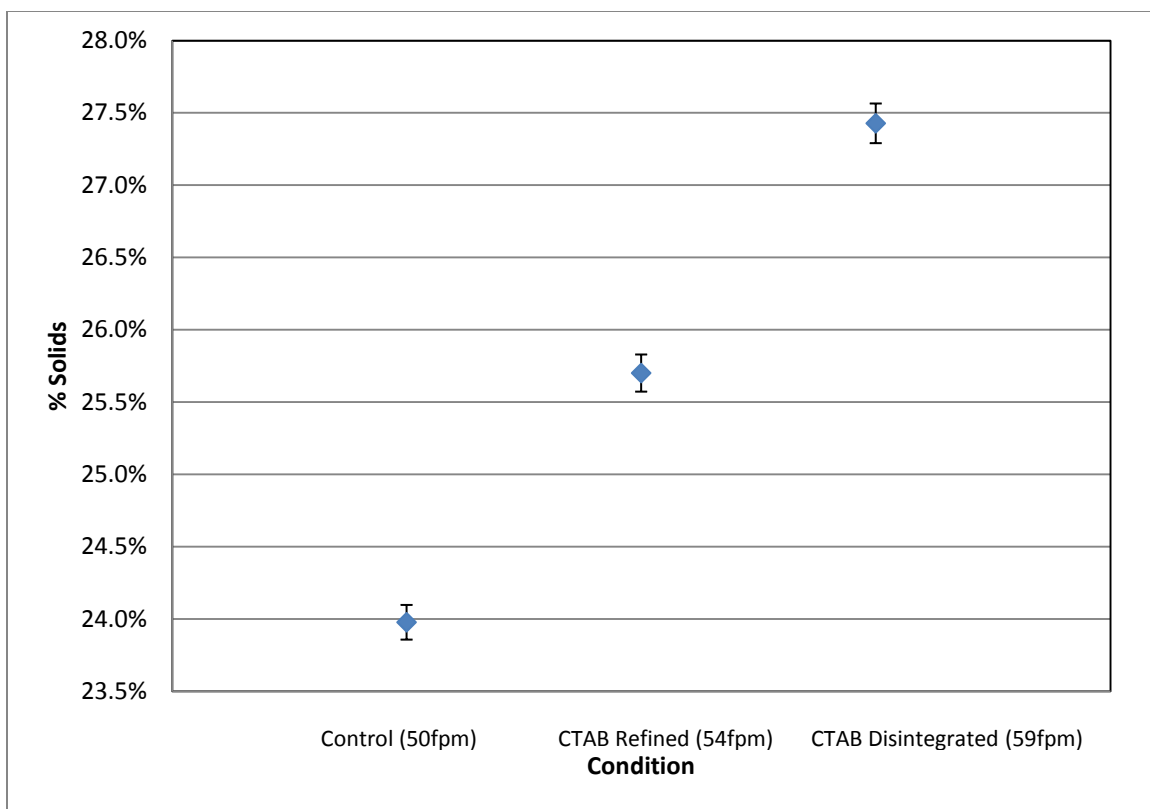


Figure 5.17. Sheet solids off the couch roll for CTAB addition point conditions.

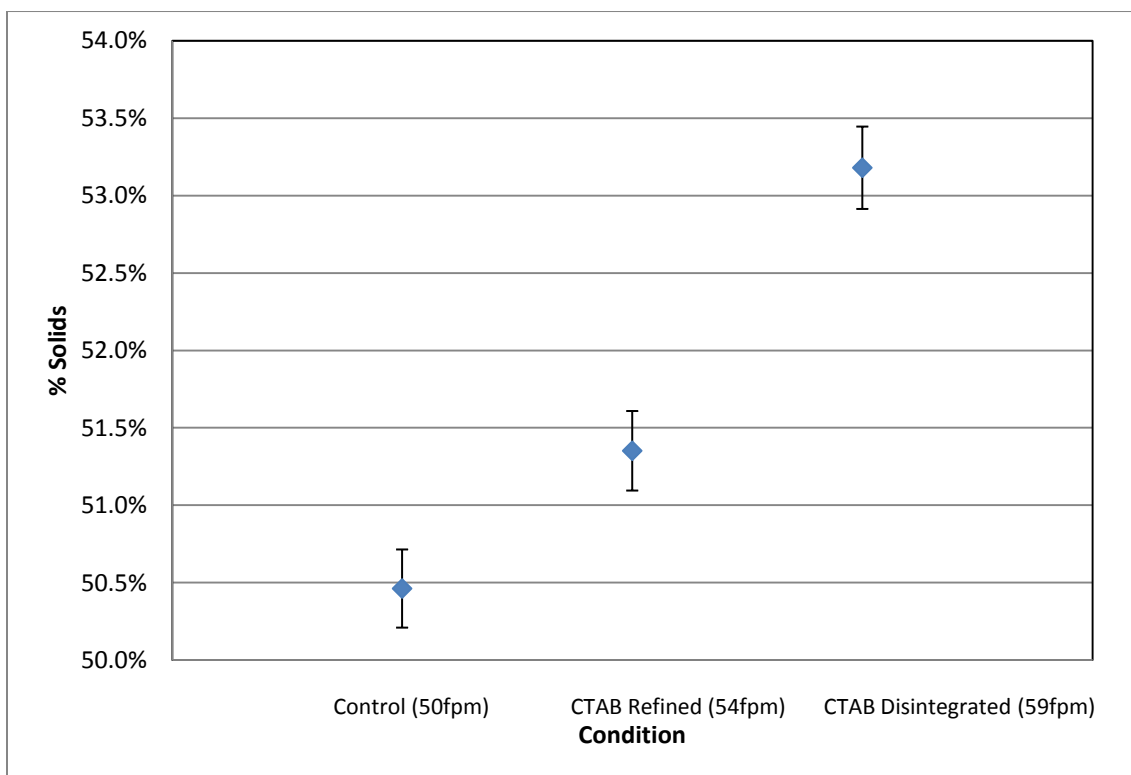


Figure 5.18. Sheet solids off the 2nd press for CTAB addition point conditions.

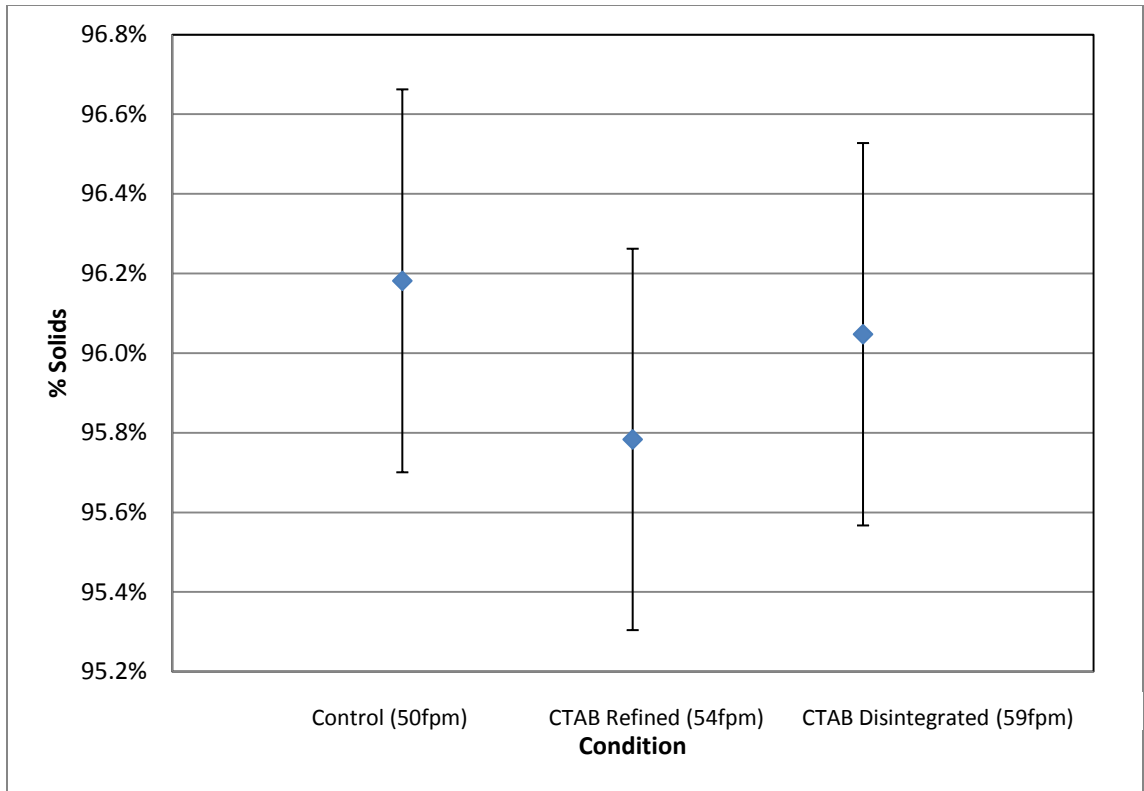


Figure 5.19. Sheet solids off the reel for CTAB addition point conditions.

It is evident from Figures 5.17 and 5.18 respectively, that there is an increase in sheet solids off the couch and exiting the second press with a change in location of CTAB addition from the refining condition to the disintegration condition. It is hypothesized that the effectiveness of CTAB is greater when its primary penetration of the fiber occurs as a function of hydration of the pulp rather than occurring post hydration through fiber penetration and adsorption deriving from a concentration gradient. It may be seen in Figure 5.19 that the addition of CTAB in the disintegration condition achieved an increase in machine speed of 9 ft/min (or 18%) compared to the control condition while maintaining reel solids. It is also noted that the press solids for the disintegration condition were approximately 3% higher than the control press solids (Figure 5.18). Based upon the accepted

relationship between press solids and machine speed (Section 4.2.1), this suggests that a further 12% increase in machine speed may have been obtainable.

Mutek total charge and streaming potential measurements were performed on headbox samples to monitor the effect of CTAB addition on slurry charge, the relevant data for all trial conditions are presented in Figure 5.20. It is evident from Figure 5.20 that the headbox charge went from negative for the control and Telioform additions to cationic (positive values) for all conditions in which CTAB was present.

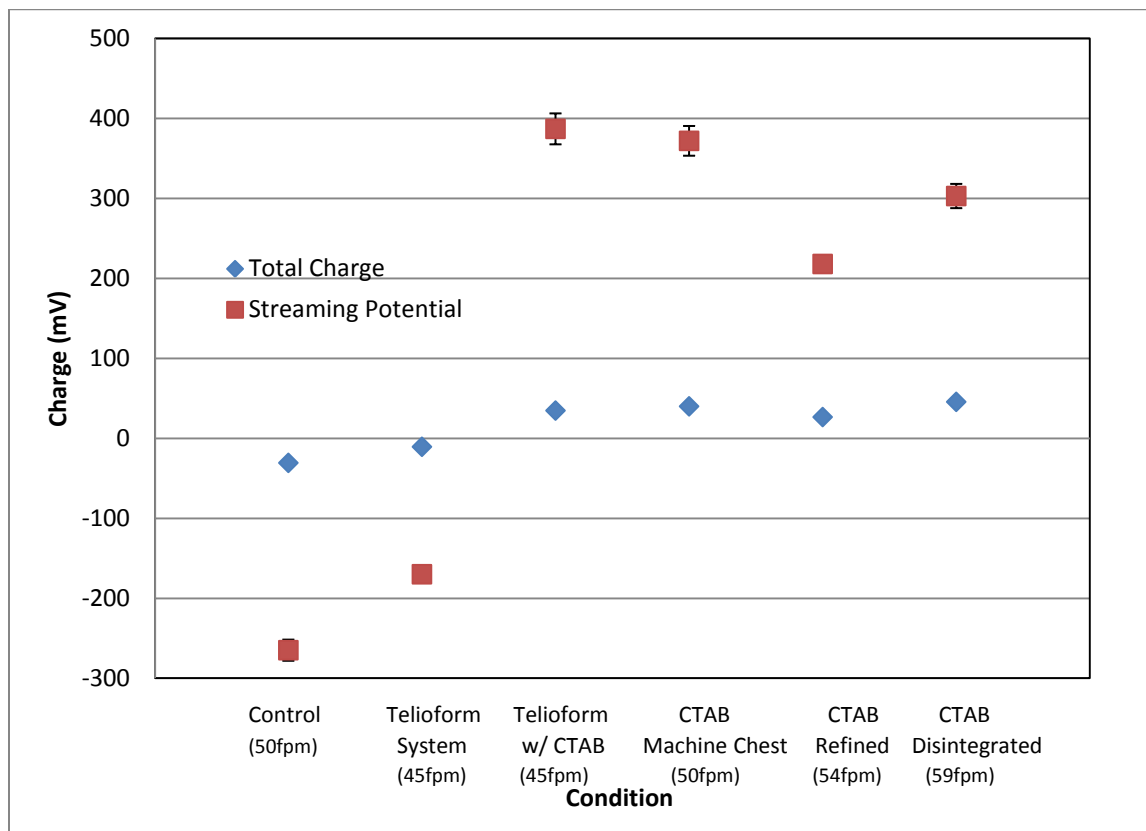


Figure 5.20. Headbox charge and streaming potential versus trial conditions.

Surface tension measurements of headbox samples for each trial condition were performed and are presented in Figure 5.21. Investigation of Figure 5.21 reveals that the addition of solely CTAB resulted in a decrease of the surface tension

by ~15 dynes, not a surprising result given the interfacial activity of the surfactant. It is noted that the surface tension of the disintegrated trial condition appears to be slightly higher than that of the machine chest and refined conditions (although statistically similar). If real, this rise in surface tension would correlate with a decrease in the amount of CTAB present at the air/water interface and hence an increase in the quantity of CTAB located on, or within the fiber, or in bulk solution.

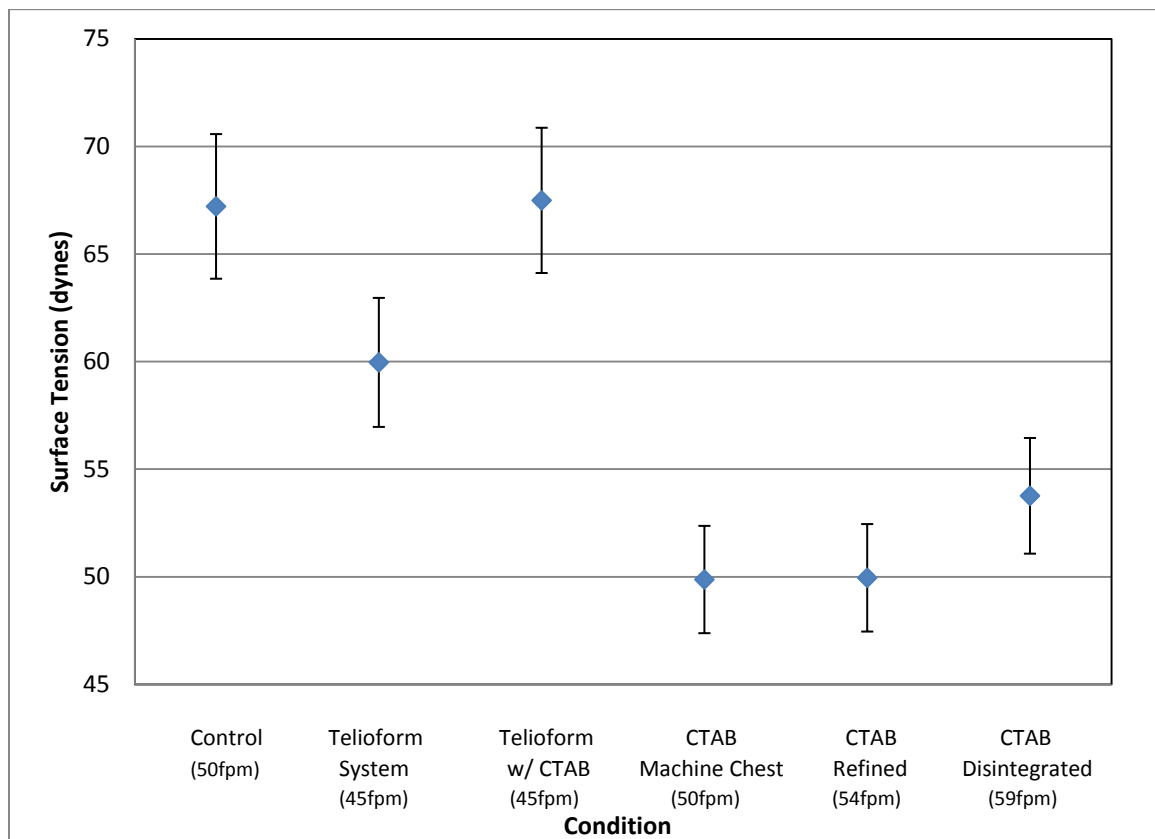


Figure 5.21. Surface tension measurements at each pulp condition.

One liter samples taken during the trial were analyzed via ATR-IR to determine the solution concentration of CTAB. This testing yielded a consistent solution concentration of approximately 2×10^{-5} M of CTAB for all CTAB containing trial conditions. If indeed the concentration of CTAB at the air/water interface was lower for the disintegration trial condition relative to the other CTAB containing

conditions, the observation of a comparable solution concentration suggests that the amount of CTAB on or in the fiber may be greater. If this hypothesis is correct, one would expect to see a greater total positive charge for the disintegrated condition versus the refined trial condition. Indeed this is observed in the data presented in Figure 5.20. To ascertain if CTAB redistribution occurred on a longer timescale, total charge and streaming potential data of the headbox samples were examined several days after the trial, the resultant data is presented in Figure 5.22.

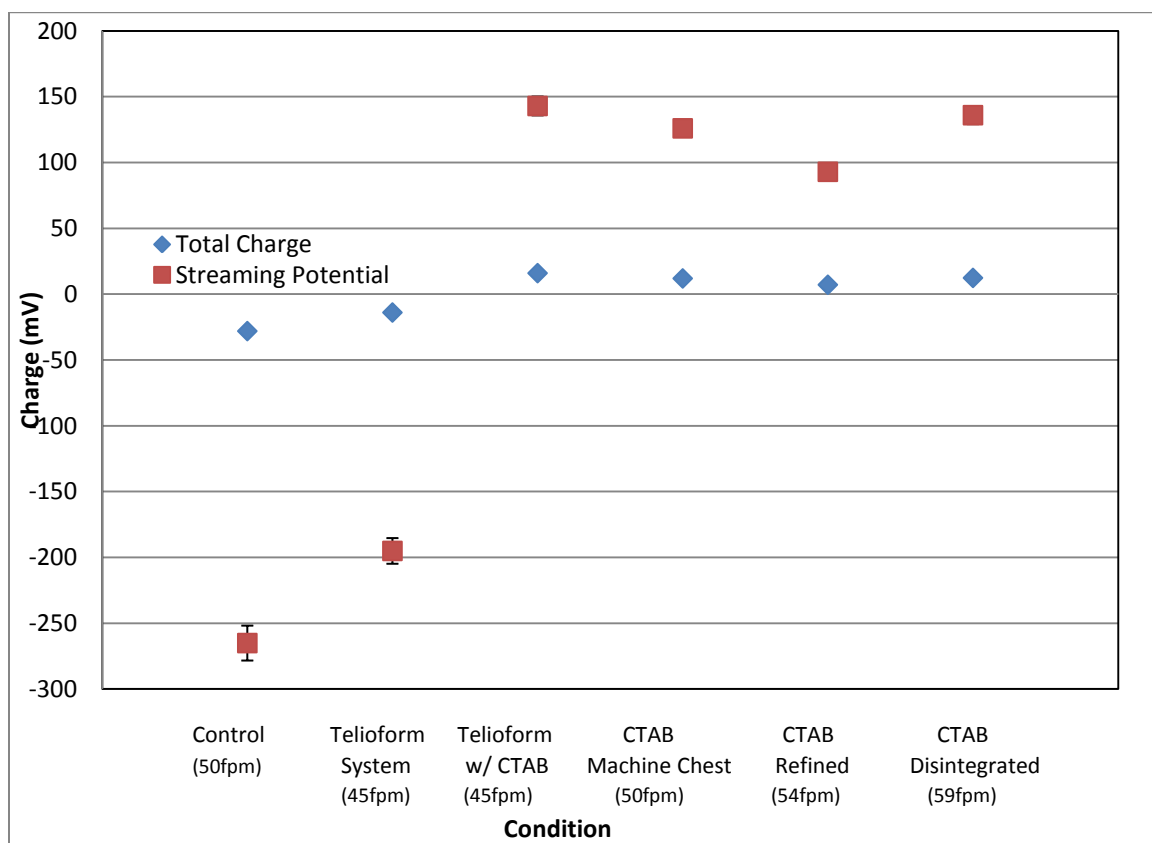


Figure 5.22. Headbox charge and streaming potential versus trial condition post trial.

A significant decrease in the total charge of the system is observed in Figure 5.22 relative to the initial data of Figure 5.20. The decrease in charge may potentially be attributed to CTAB progressively traveling further into the fiber and

becoming inaccessible to the titration. Correlated ATR-IR and surface tension analysis was performed on these samples and resulted in nearly identical data to that acquired during the trial.

During the machine trial pulp samples were taken at the head box for WRV testing to compare machine performance to laboratory scale preparation methods. Figure 5.23 presents the WRV data acquired during the trial.

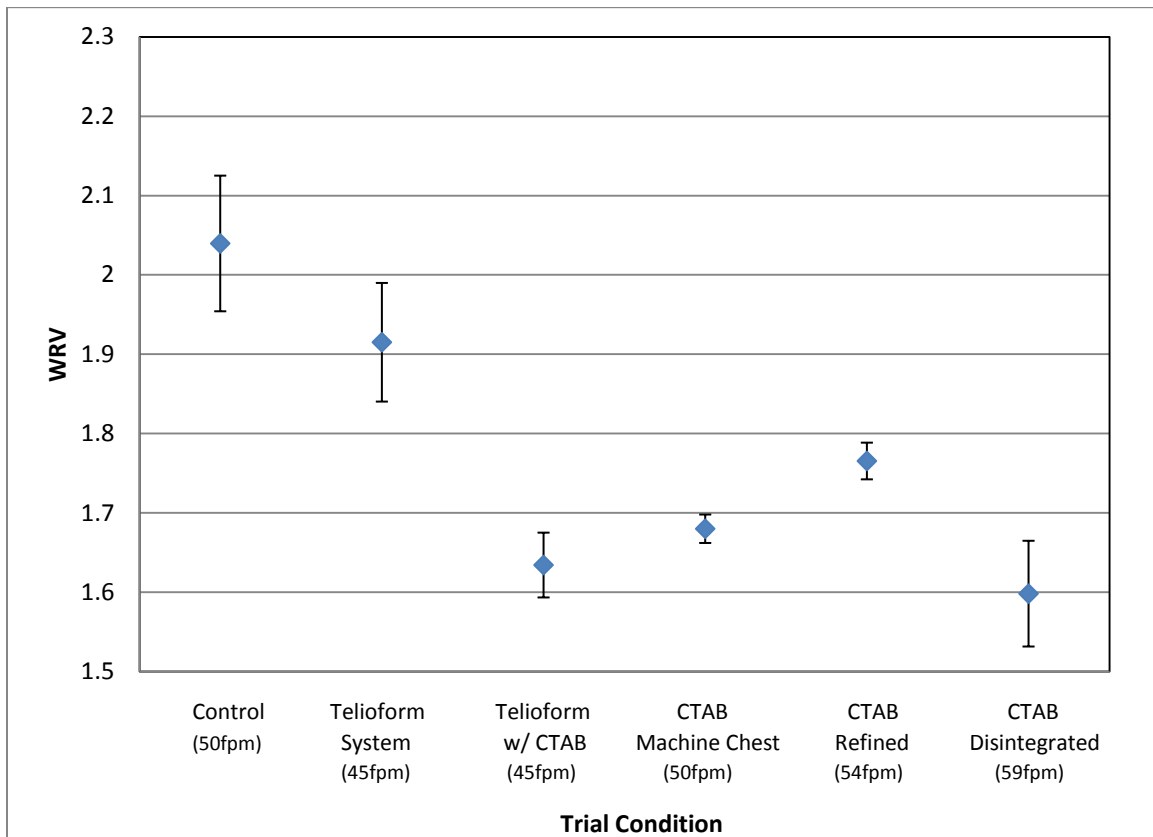


Figure 5.23. Trial WRV data employing head box samples.

Examination of Figure 5.23 indicates that WRV testing predicted that the Teloform/CTAB condition should have resulted in enhanced dewatering and corresponding increases in machine speed; however, this was not realized during the trial. A discrepancy also exists in the WRV results of the CTAB refining condition

where the WRV was the third highest, yet, the machine speed during the condition was the second fastest. These two observations suggest that while WRV testing provides good insight into expected forming and pressing behavior, actual machine performance may differ substantially.

Sheets produced during each trial condition were characterized in terms of their physical properties, specific parameters examined were; sheet strength (tensile) in both the machine and the cross machine directions, z-directional strength (Scott bond), sheet thickness, and sheet pore volume and distribution. Sheet tensile data for the machine direction and the cross machine direction are presented in Figures 5.24 and 5.25, respectively.

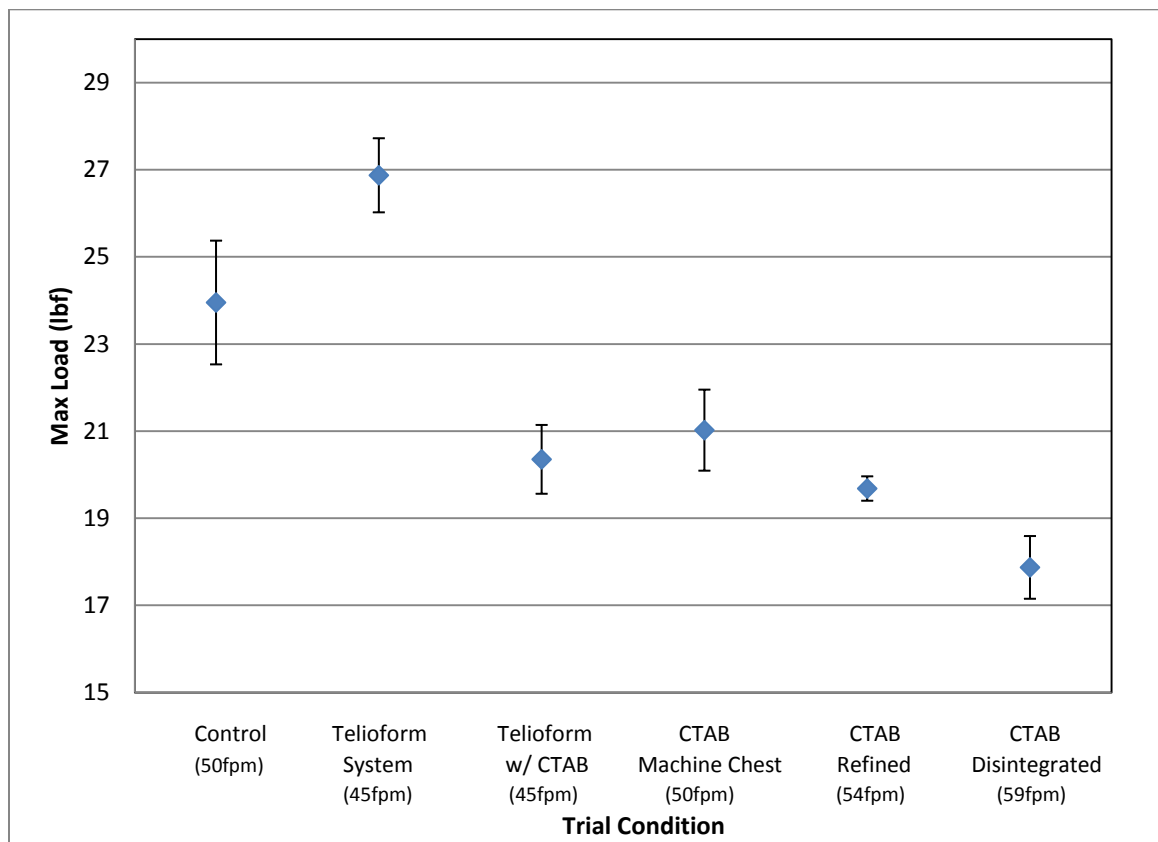


Figure 5.24. Sheet tensile for each trial condition in the machine direction.

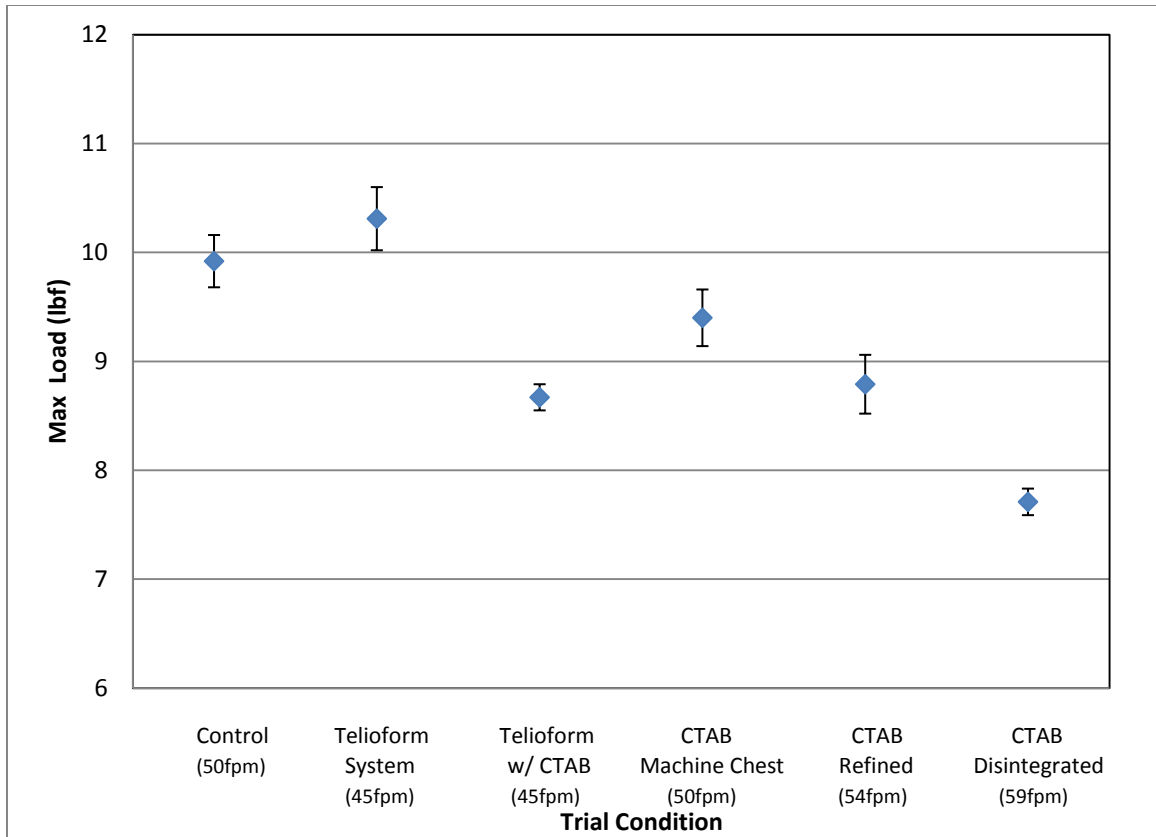


Figure 5.25. Sheet tensile for each trial condition in the cross machine direction.

The sheet tensile data of Figures 5.24 and 5.25 clearly indicate that the sheet lost significant strength relative to the control condition upon addition of CTAB to the system. The observed sheet strength loss corresponds with the laboratory data of Chapter 4. A comparable trend to that observed for sheet tensile was observed for z-direction strength as presented in Figure 5.26.

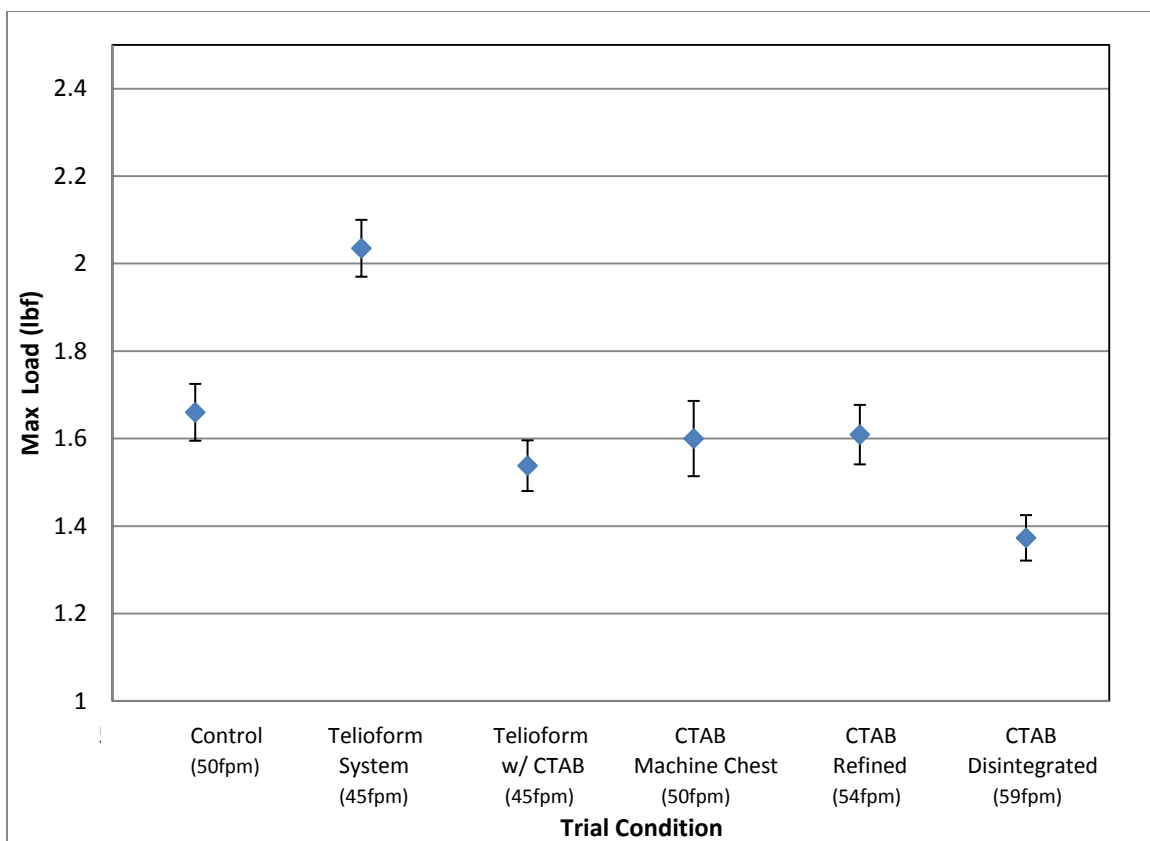


Figure 5.26. Sheet z-directional strength for each trial condition.

The stiffness of the resultant sheets was also examined and displayed a trend similar to that of the strength data. Specifically, stiffness decreased from a control value of 5.05 stiffness units to a value of 3.98 stiffness units (~20%) for the 1 wt% CTAB disintegrated condition.

The thickness of the sheet was examined in order to determine if there was a relationship between sheet thickness and strength loss. Sheet caliper is presented in Figure 5.27 for each trial condition.

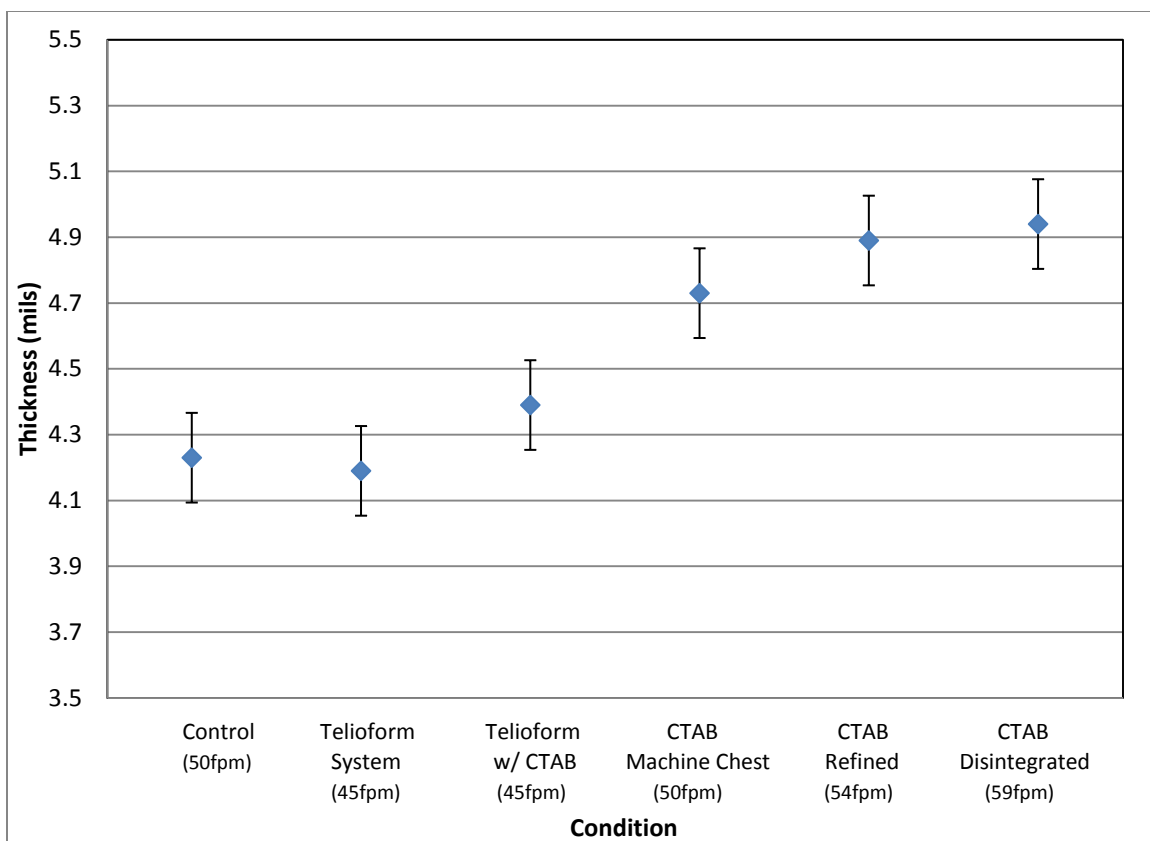


Figure 5.27. Sheet thickness for each trial condition.

Examination of the data of Figure 5.27 reveals that there is a significant increase in the sheet thickness in all conditions containing CTAB, a finding that is consistent with the data of Section 4.2.11. Indeed, addition of solely CTAB resulted in an increase of approximately half a mil in thickness of the sheet relative to the control. The pore size and distribution of the sheet was characterized via mercury porosimetry and is presented in Figure 5.28 in the form of log differential pore volume versus log pore diameter for each trial condition.

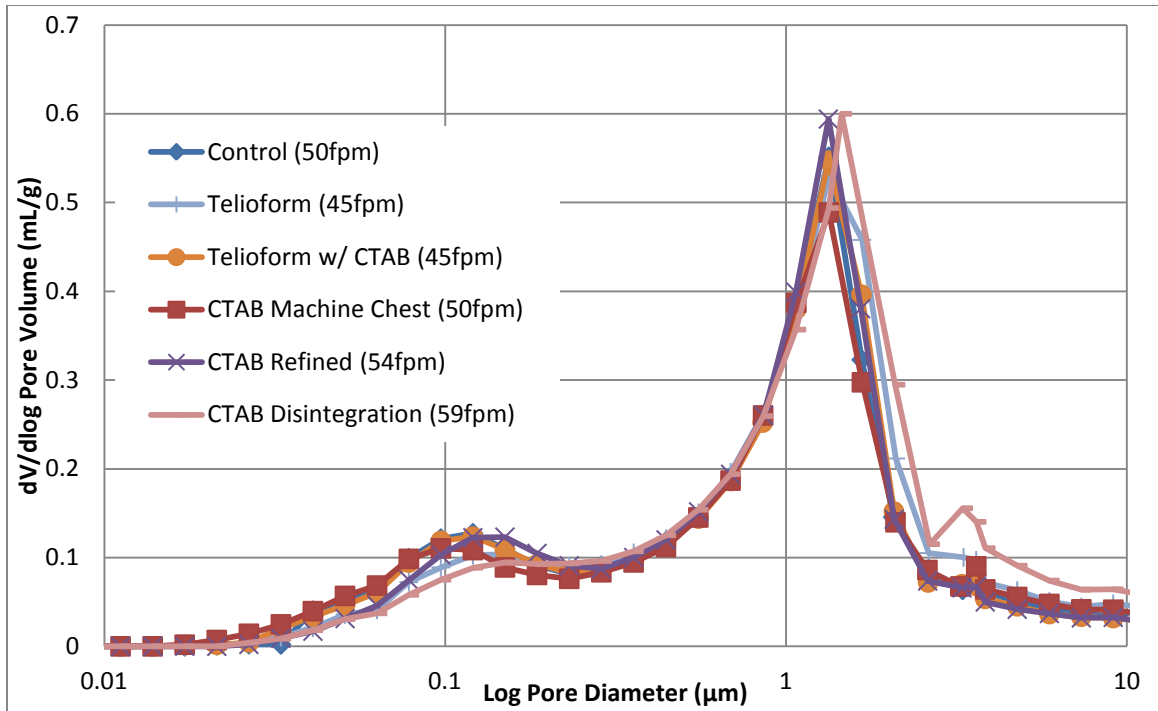


Figure 5.28. Log differential pore volume versus log pore diameter for each trial condition.

Examination of the porosimetry data of Figure 5.28, reveals that the addition of CTAB shifts the average pore size to larger pore diameters, whilst also increasing the total pore volume. For CTAB addition in the presence of Telioform, the increase in total pore volume is reduced relative to solely CTAB addition, however the shift to larger pores is maintained.

The formation of the sheet was analyzed for all trial conditions by measurement of the Kajaani Formation Index, and the floc distribution. The resultant data are presented in Figures 5.29 and 5.30, respectively.

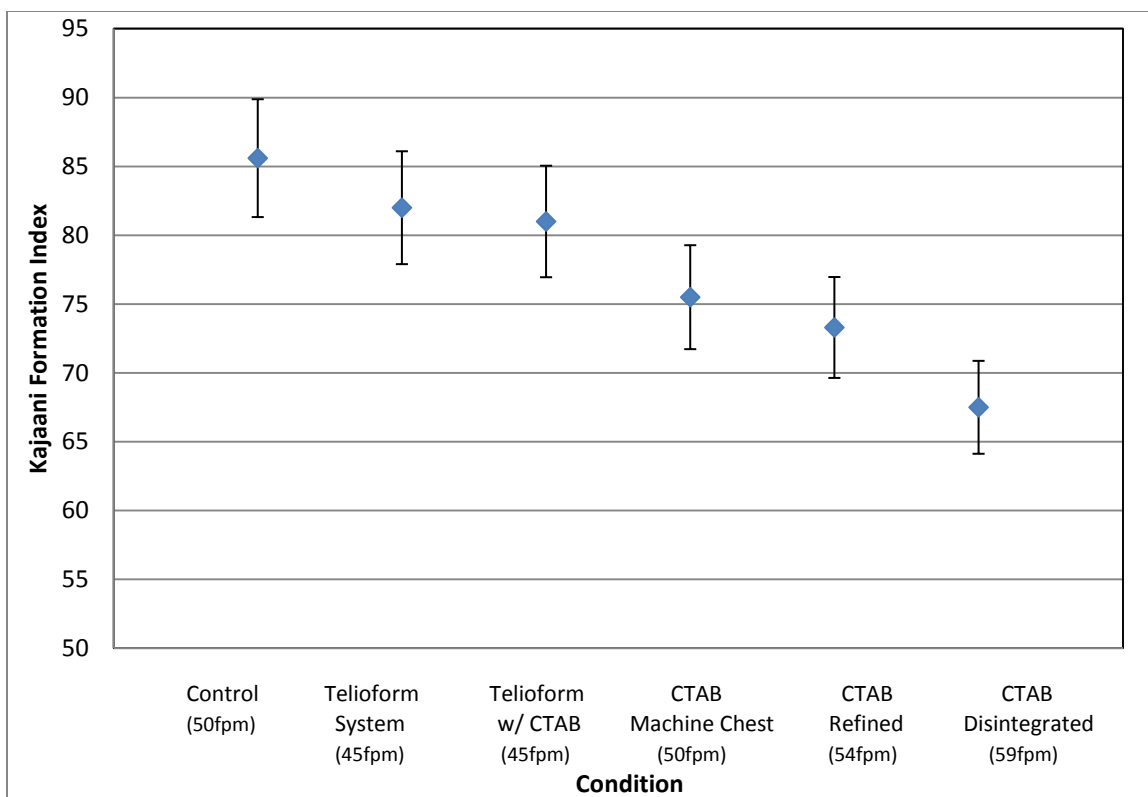


Figure 5.29. Kajaani formation index of paper samples for all trial conditions.

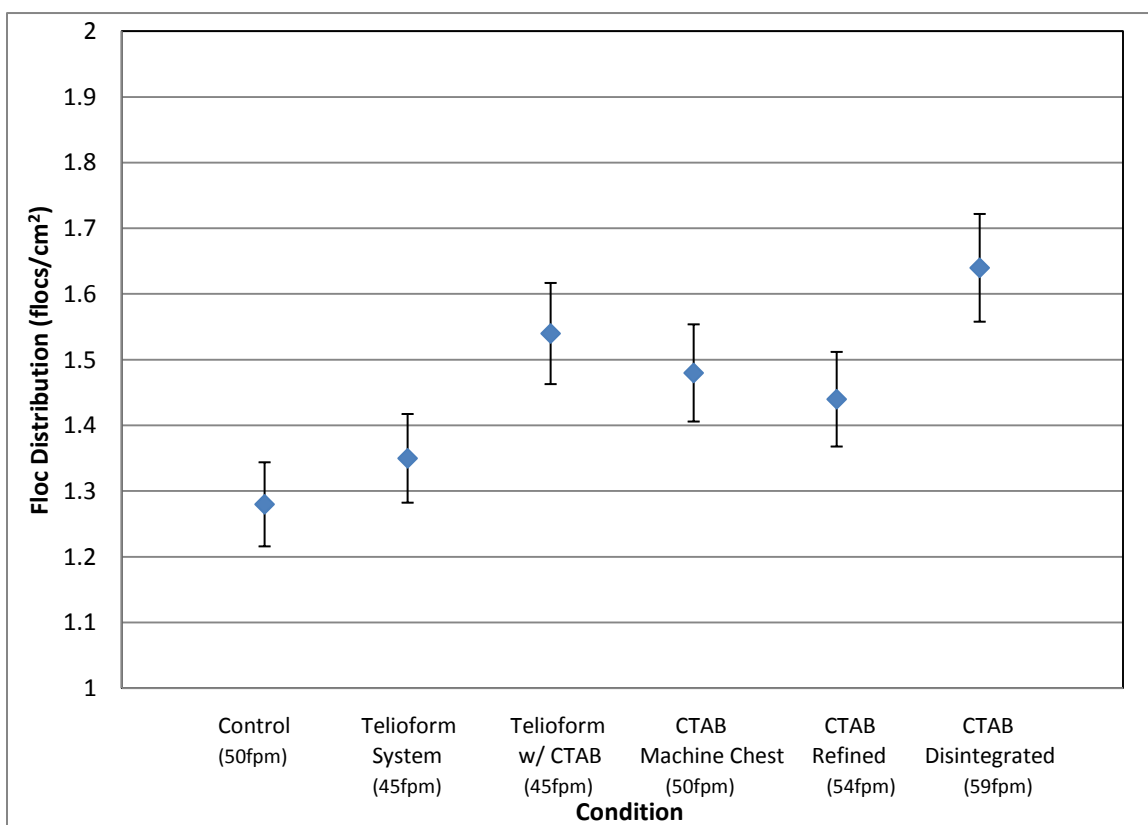


Figure 5.30. Floc distribution of paper samples for all trial conditions.

It is evident from examination of the data of Figure 5.29 that the addition of CTAB significantly decreased the Kajaani Formation Index (KFI), and further, that the lowest value correlates with the best dewatering condition (disintegration). The decreasing KFI is interpreted as an opening up of the sheet due to the breaking up of existing floc structures, or more likely, the prohibition of them from forming due to electrostatic repulsion. The floc formation behavior is consistent with knowledge that the fiber is positively charged through the adsorption of CTAB and hence experiences electrostatic repulsion. The data of Figure 5.30 indicates that CTAB addition generated a greater floc distribution, that is, a greater number of smaller flocs per unit area, a finding consistent with the KFI data and the enhanced water removal observed.

5.4. Economic Analysis

Within the papermaking industry it is generally accepted that dryer savings may be translated into production increases, and given that most machines run dryer limited the ability to create dryer savings would have broad applicability in the industry (Bilodeau 2009). Translating the reduction of water into the dryer section into increased dryer capacity (via a mass balance presented in Section 4.2.1) demonstrates that an increase in press solids of 4% yields approximately a 15.5% increase in dryer capacity (~1:4 ratio). Assuming an equivalent scaling from the pilot machine to a full scale paper machine, the 18% dryer capacity increase demonstrated in Section 5.3 would correlate with a production rate increase of 18%. By increasing the production of the machine by 18%, the fixed cost per ton of

paper is distributed over a greater amount of paper, which decreases energy, labor, and capital cost per ton of paper. Raw material and additive costs (exclusive of CTAB) remain fixed due to a ton of paper requiring a ton of material to be produced. To evaluate this mass balance with cost included, a model was constructed in a Microsoft Excel spreadsheet presented in Figure 5.31.

Production Rate						
Machine Width	25	ft		CTAB Dosage (wt%)	1	
Machine Speed	3000	ft/min		CTAB Cost Per Pound	\$ 1.52	
Basis Weight	30	lb / 3000 ft^2		Production Improvement	18%	
Reel Moisture	5	% moisture				
Total OD production	712.5	lb/min				
		Control	With CTAB			
Materials Cost Per Ton	\$ 500.00	\$ 530.40				
Fixed Cost (labor, energy, etc)	\$ 200.00	\$ 169.49				
Total Cost Per Ton	\$ 700.00	\$ 699.89				
Value per ton	\$ 800.00	\$ 800.00				
	Daily Production			Additional Profit		
	Tons	Cost	Value	Daily Profit	Daily	Annually
Control Costing	513.00	\$ 359,100.00	\$ 410,400.00	\$ 51,300.00	\$ -	\$ -
CTAB Costing	605.34	\$ 423,672.34	\$ 484,272.00	\$ 60,599.66	\$ 9,299.66	\$3,394,377.36

Figure 5.31. Production and profit analysis model. Microsoft Excel calculation demonstrating ~\$3.4 million profit increase with an 18% production increase in the presence of 1wt% CTAB.

Industrial estimates were employed as a basis for calculations determining the economic effect of increased production via CTAB dosage at 1 w% with a cost of \$1.52 per pound for the surfactant. The CTAB cost per pound was determined via purchase quotes acquired by Armstrong World Industries. Utilizing a raw material cost of \$500 per ton, fixed costs of \$200 per ton, and a sale value of \$800 per ton (Bilodeau 2009) on the same hypothetical paper machine previously described in Section 4.2.1; an increase of 18% in production yields an annual net profit increase of nearly \$3.4 million. Using this methodology, it is possible to demonstrate that at

\$1.52 per pound for the additive, on this machine a break even scenario requires a minimum production increase of approximately 12%, which relates to an increase in press solids of approximately 3%. This minimum however is heavily dependent on each specific machine and grade of paper, since the fixed cost per ton, material cost per ton, value per ton, and additive cost and dosage will vary greatly.

5.5. Conclusions

Data from the second machine trial supported the laboratory based findings that the addition of CTAB to a pulp slurry significantly improves water removal in the paper making process. Indeed the most favorable trial condition resulted in a production increase of 18% with the measured press solids suggesting a further 12% production increase may have been achievable. These realized and unrealized production gains easily allow the technology to be economically viable. It is noted however, that the technology results in a significant loss of sheet strength. It is likely that CTAB resident on the fiber surface inhibits fiber-fiber hydrogen bonding required for sheet strength. In addition, electrostatic repulsion of fibers due to reversal of the charge of the system by CTAB results in bulking of the sheet and further inhibits fiber-fiber bonding. The resultant changes in fiber distribution with the sheet creates an increased pore volume and a shift to larger pore sizes in the presence of CTAB, leading to enhanced dewatering. As may be expected however, the formation of the sheet is negatively impacted by the addition of CTAB.

Mutek system charge, ATR-IR measurement of solution concentration, and surface tension data suggest that a greater quantity of CTAB is located on or within

the fiber when the surfactant is added in the disintegration step of slurry preparation, as opposed to addition during refining or at the machine chest. As such the most favorable addition for CTAB was observed during disintegration. These results mirror those acquired in bench top experimentation and therefore represent a successful translation of the technology to the pilot scale. It is noted however that attempts to employ CTAB in conjunction with a commonly used formation, drainage, and retention system (Telioform) were largely unsuccessful, and did not demonstrate improvements seen on the bench scale. Examination of tray solids in the Telioform conditions led to the conclusion that upon CTAB addition to the system the retention chemistry was disrupted (tray solids increased in the presence of CTAB illustrating a loss of retention). It was hypothesized that the shorter residence times on the pilot machine, in comparison to the bench scale, CTAB competed with the cationic component of the Telioform system in combining with bentonite; leading to a hindering of both mechanisms.

CHAPTER 6

EXAMINATION OF CTAB AND BENTONITE CO-ADDITION

The loss of sheet strength observed upon the addition of CTAB to the papermaking slurry is a result that many manufactures would find unacceptable since many grades of paper, and paper products, are sold on a strength basis. In addition, the observed decrease in surface tension, and increase in sheet bulk, are potential barriers to the technology's implementation in a production environment. In an attempt to mitigate these negative effects, an anionic scavenger was employed with the objective of removing CTAB resident on the exterior of fiber surfaces to determine if the surfactant was giving rise to bulking and decreasing fiber-fiber hydrogen bonding. Additionally the scavenger was intended to remove CTAB from the air/water interface and thereby raise the surface tension. Specifically, bentonite clay was added to slurries containing CTAB with the intent that the anionic charge of its platelet faces would electrostatically scavenge the cationic surfactant. Figure 6.1 presents WRV data arising from sequential addition of CTAB, followed by bentonite at 4 wt% after 2 minutes of agitation.

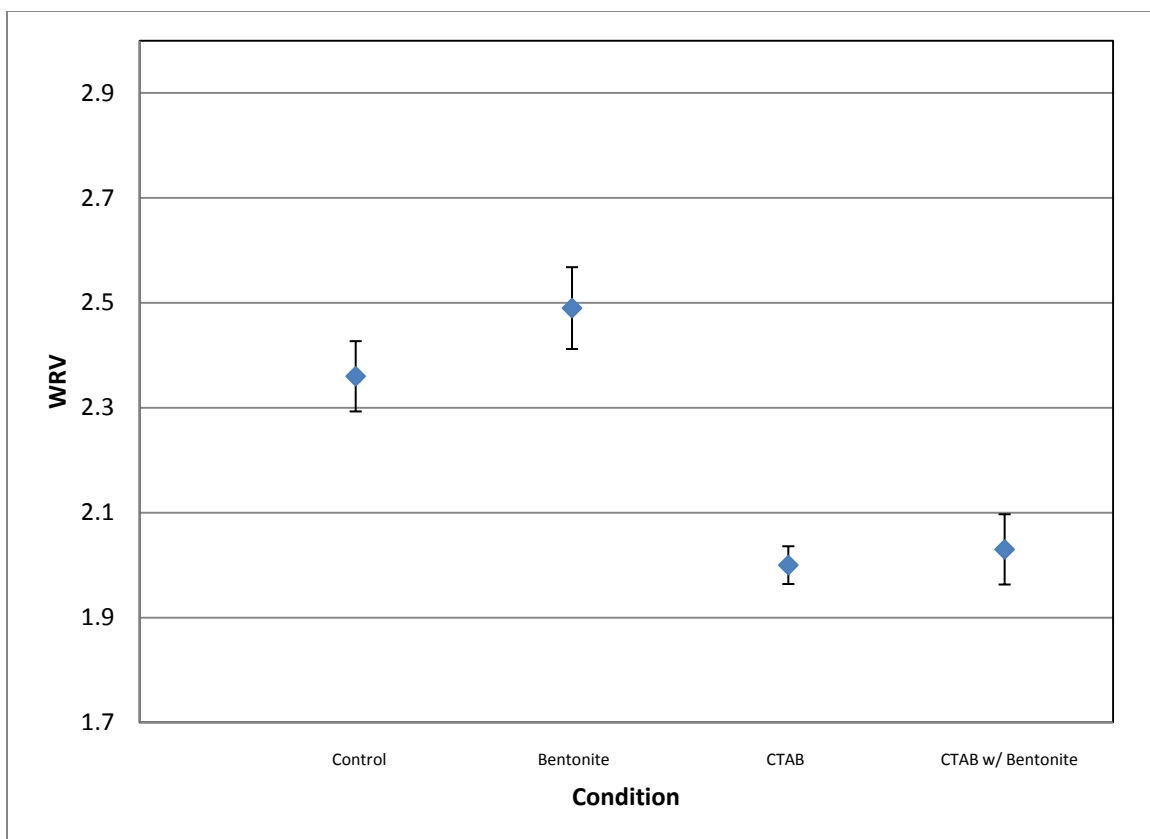


Figure 6.1. WRV of control conditions, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

Importantly, it is evident from Figure 6.1 that the addition of bentonite post CTAB has no apparent impact on the positive effect of CTAB reduction of the WRV. In order to determine if bentonite addition scavenged CTAB from the air-water interface, the surface tension of the pulp was measured as a function of CTAB and bentonite addition, the resultant data are presented in Figure 6.2.

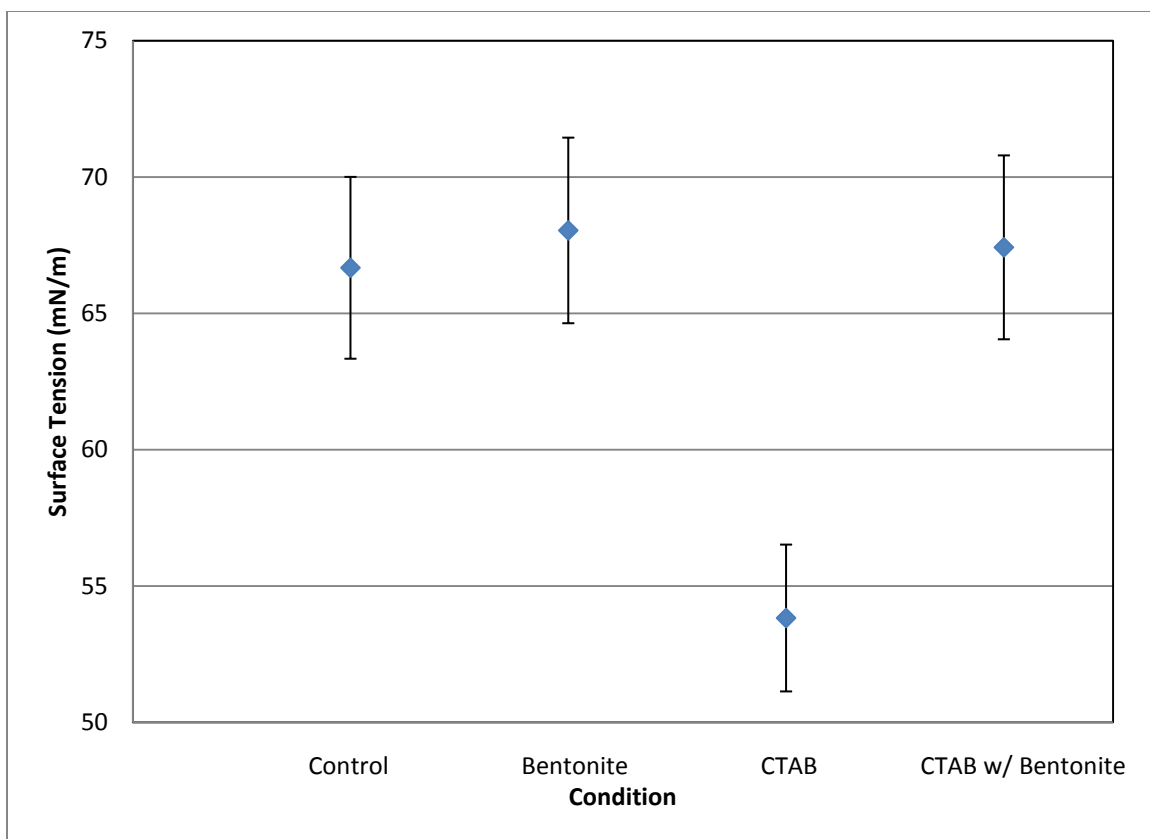


Figure 6.2. Surface tension of control conditions, the addition of 1wt% CTAB, and subsequent addition 4wt% bentonite.

Figure 6.2 illustrates that the decrease in surface tension arising from the addition of CTAB may be reversed by the post addition of bentonite. Consequently the data of Figure 6.2 demonstrates that in fact bentonite is capable of scavenging CTAB, at least from the air-water interface.

The results of Figure 6.2 suggest that pad thickness may also be expected to be modified by the sequential addition of CTAB and bentonite. An experiment probing the potential effect was performed and the resultant data are presented in Figure 6.3.

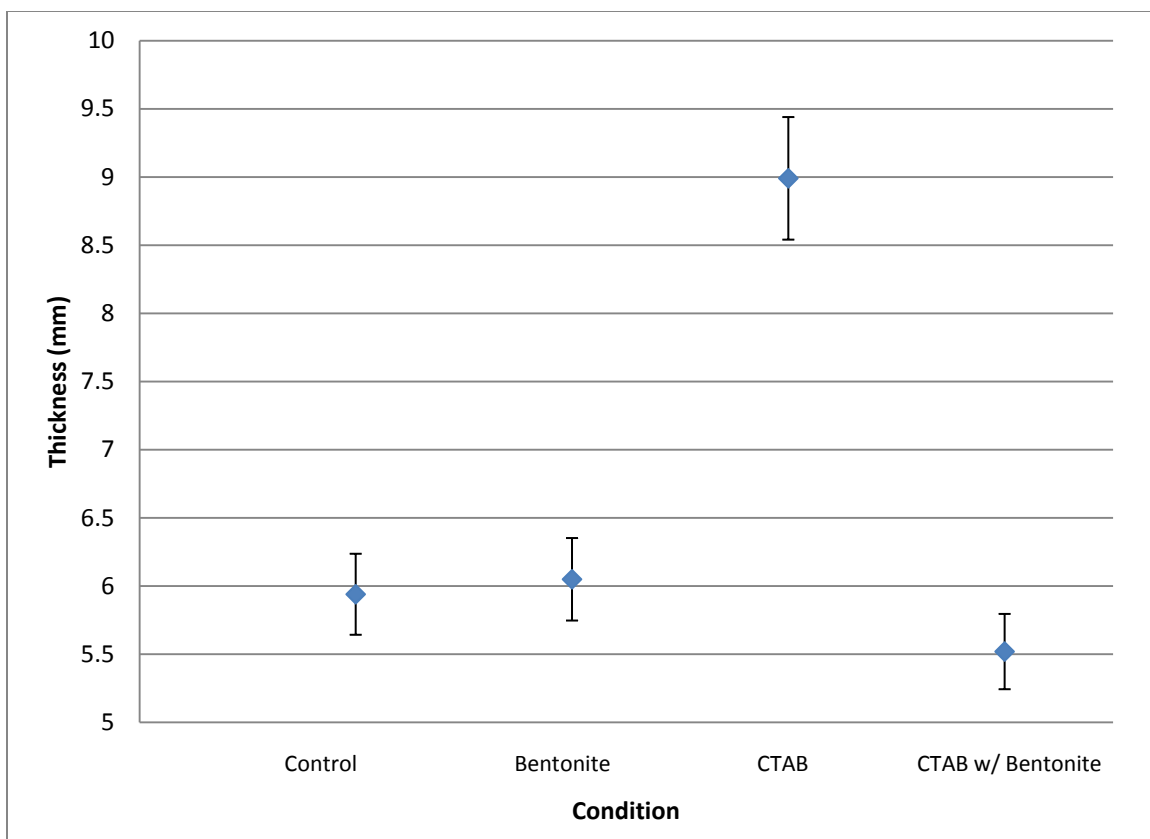


Figure 6.3. WRV Pad thickness of control conditions, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

The data of Figure 6.3 depict a reduction in the WRV pad thickness after bentonite addition to a CTAB treated pulp, indeed the thickness returns to that of the control conditions. Since the data of Figure 6.3 indicate a change in total pore volume, and the pore size distribution, or both, upon sequential addition of CTAB and bentonite, mercury porosimetry was employed to evaluate the WRV pads. The resultant data are presented in Figure 6.4.

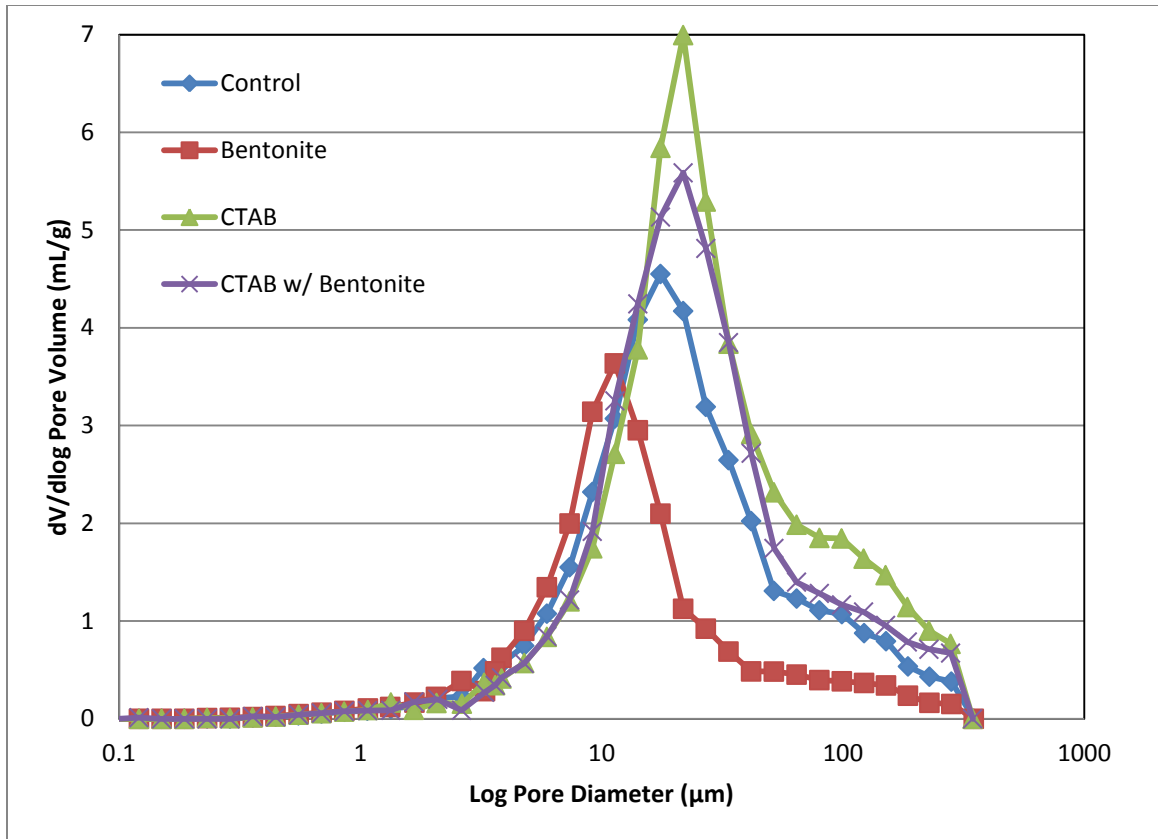


Figure 6.4. Mercury porosimetry of control conditions, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

Investigation of Figure 6.4 reveals that the addition of bentonite to a CTAB treated pulp results in a decrease in the total pore volume, but does not completely negate the increase in pore radius resulting from CTAB addition. Further examination of Figure 6.4 demonstrates that for both the CTAB addition and the sequential CTAB/bentonite addition, an increase to larger pore sizes is evident, as is a narrowing of the overall distribution. This suggests that in both cases enhanced water removal may be attributed to the pore size distribution. In fact analysis by MacGregor (1998) indicated that the pores with the largest and smallest diameters dominated the rate of water exiting a fiber mat. As such a narrowing of the

distribution should increase the rate of water removal; likewise a shift of the pore distribution to larger pores will result in a similar phenomenon.

Finally, the effect of bentonite addition to CTAB treated pulps on the tensile strength of the resultant paper was tested; the results are presented in Figure 6.5.

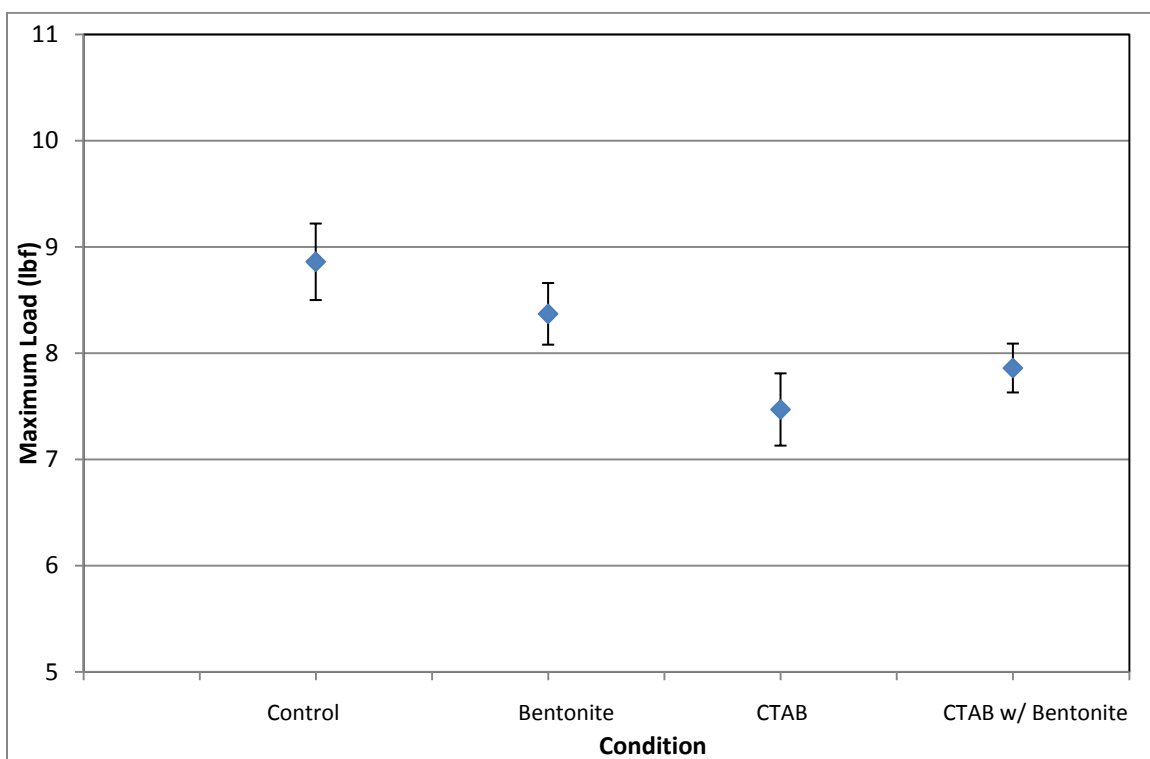


Figure 6.5. Tensile of control conditions, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

It is evident from Figure 6.5 that only a marginal recovery of the sheet tensile strength resulted from the addition of bentonite to a CTAB dosed slurry. A possible mechanism is that bentonite with absorbed CTAB may be retained within the fiber mat and hinder the hydrogen bonding required for sheet strength. If this theory is correct, the ash content of the sheet should be greater for the sequential CTAB/bentonite addition condition. As such sheet ash content was determined; the resultant data are presented in Figure 6.6.

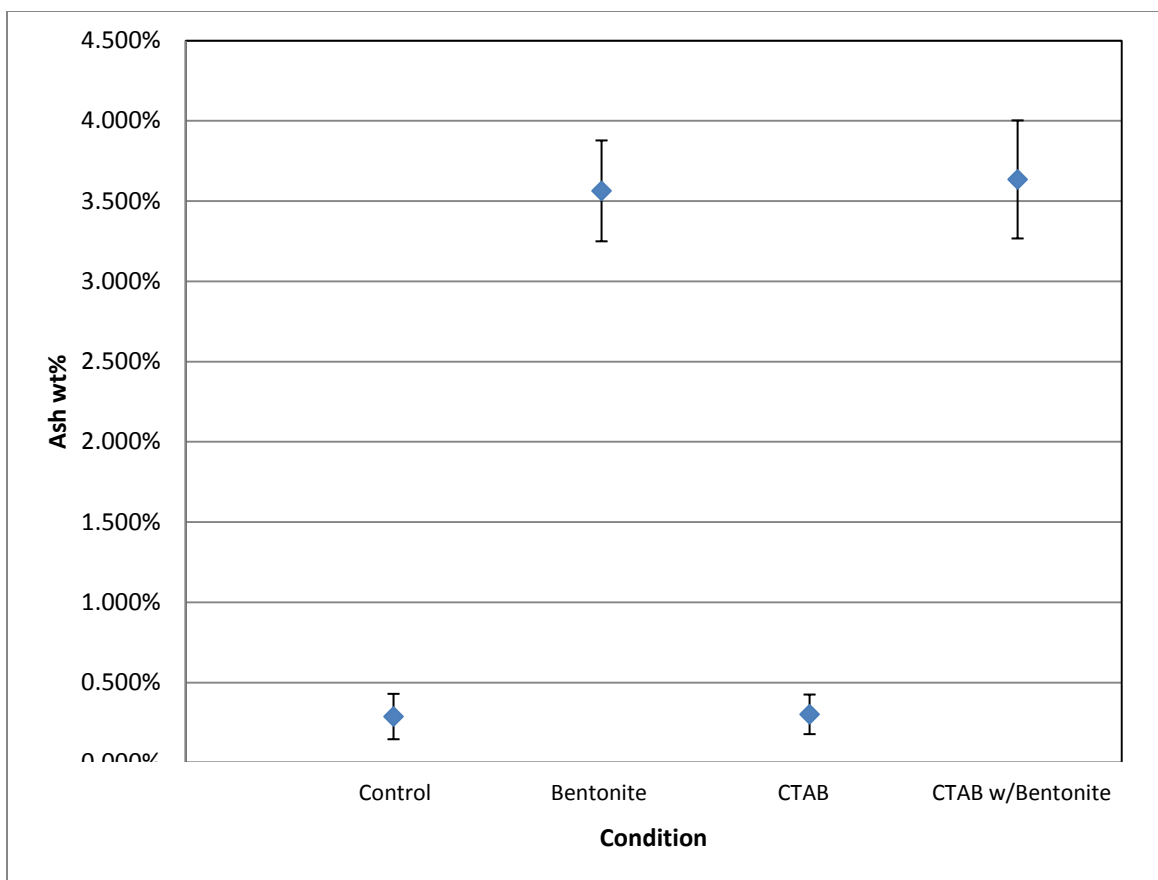


Figure 6.6. Sheet ash of control conditions, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

Not surprisingly, Figure 6.6 reveals that there was no effect on sheet ash with the addition of CTAB, the addition of bentonite on its own results in significant retention of the clay in the fiber sheet. Sequential addition of CTAB and bentonite results in statistically similar ash content as bentonite addition solely. As such the data is inconclusive in regard to the mechanism of sheet strength loss since the data of Figure 6.5 indicates that solely bentonite addition to a pulp had only a small negative impact on tensile strength. Sheet formation and floc distribution were examined to determine the effect of bentonite and sequential CTAB/bentonite addition on fiber distribution, the resultant data are presented in Figures 6.7 and 6.8.

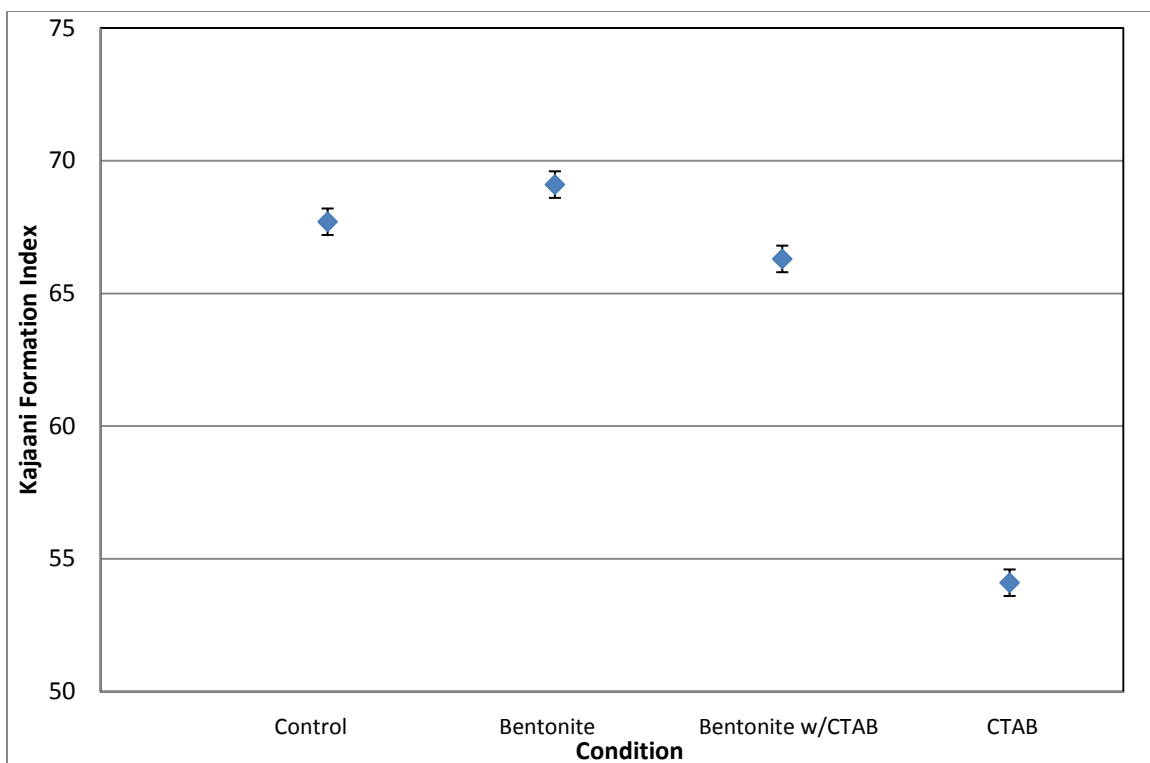


Figure 6.7. Kajaani formation indices of control conditions, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

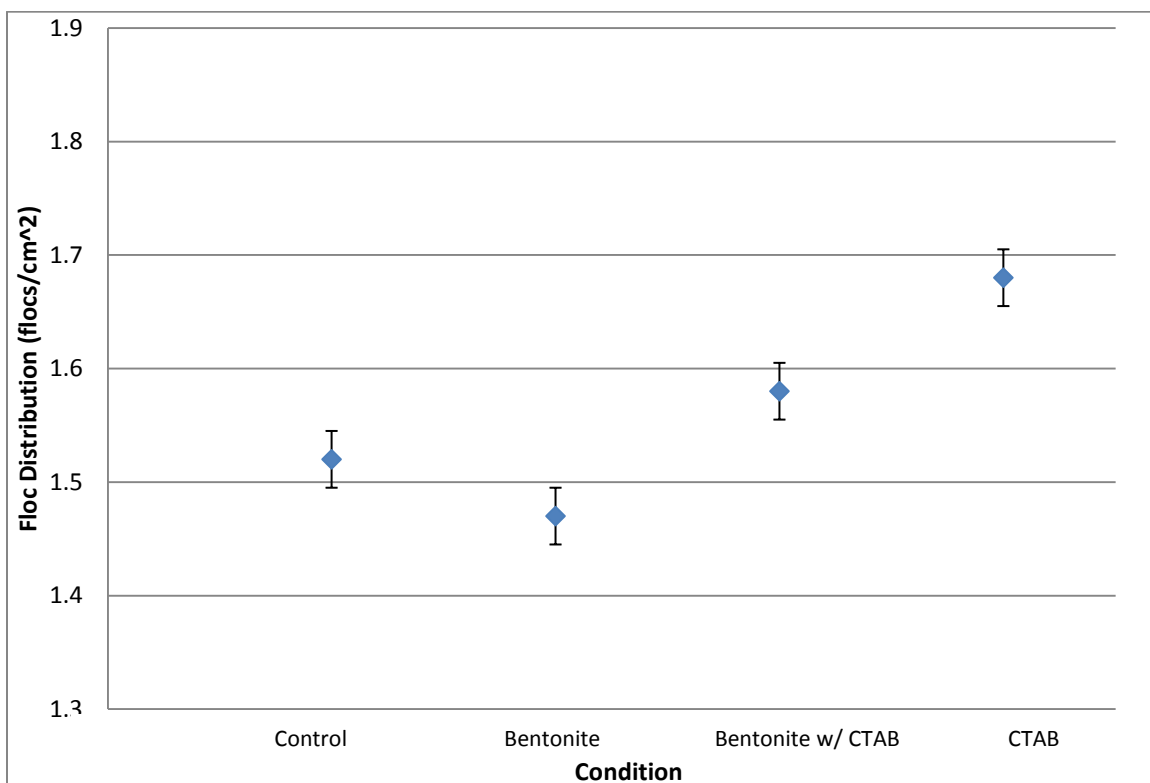


Figure 6.8. Floc distribution of control conditions, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

From investigation of the data of Figures 6.7 and 6.8, it is hypothesized that the addition of bentonite to a fiber system pretreated with CTAB results in bentonite scavenging CTAB from the fiber and partially reversing the disruption of formation of the sheet. The addition of bentonite to CTAB dosed pulps closes up the sheet, but does not completely reverse the effect of CTAB generating smaller flocs and hence enhanced dewatering. For bentonite to affect water removal as an ash or filler, 2-3 wt% of ash must be retained in the sheet (Scott 1996), a value attained in Figure 6.6. However, as bentonite is largely anionic it actually holds water in the sheet, which may be seen in Figure 6.1 for the addition of solely bentonite.

As was demonstrated in Figure 4.19, CTAB addition to pulp slurries results in the localization of the surfactant on the fiber surface, a concomitant increase in the streaming potential to positive values, and charge reversal of the system. In order to determine if bentonite addition was effective at scavenging CTAB from the surface of pulp fibers, streaming potential and total charge measurements were performed on CTAB and bentonite dosed pulps, as presented in Figure 6.9.

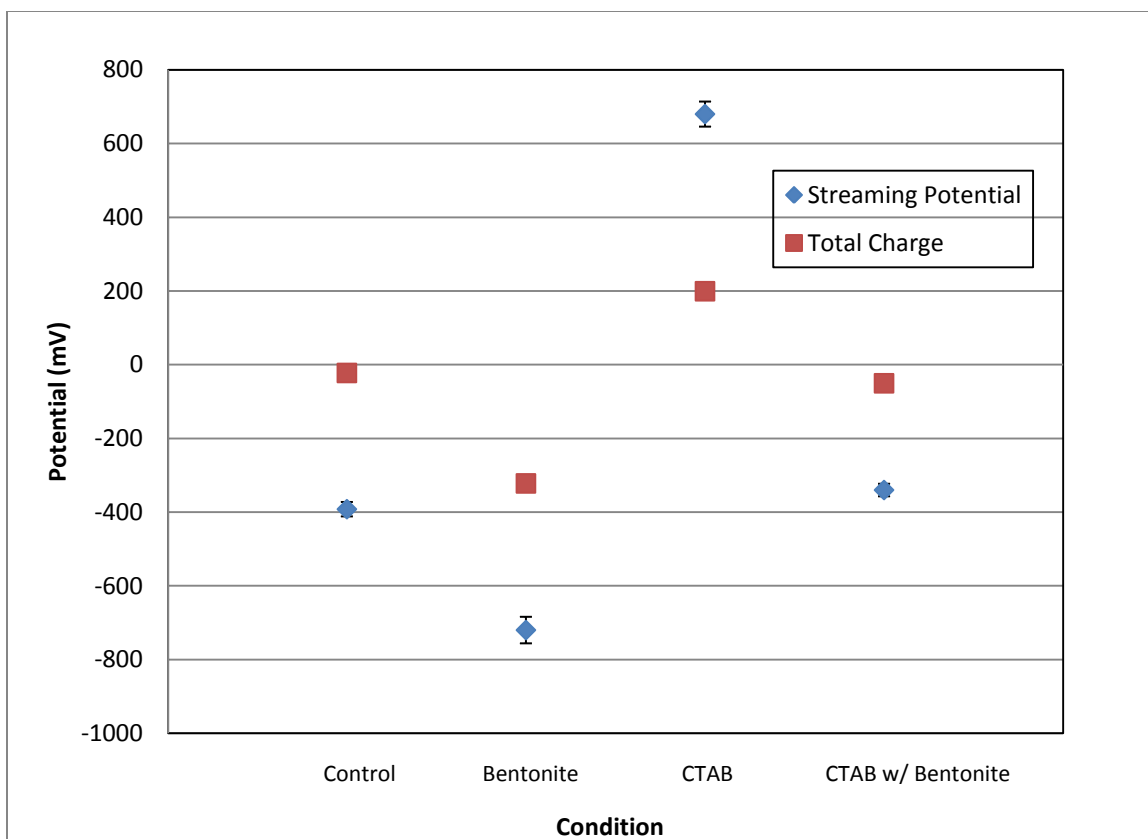


Figure 6.9. Streaming potential and total charge of control conditions, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

It is evident from Figure 6.9 that bentonite addition results in the return of the system charge to the near neutral level observed prior to CTAB addition. In addition, the streaming potential is returned to strongly negative values. This is a significant result since paper machines typically run in the negative total system charge regime, a range in which the sequential addition of CTAB and bentonite results in, whilst still providing enhanced water removal. This finding suggests that indeed bentonite is effective at scavenging bound surfactant or alternatively its contribution to the streaming potential and total charge of the system results in a return of pre-CTAB conditions.

In order to determine whether CTAB is in fact removed from the fiber by the addition of bentonite, the number of available hydroxyl groups on cellulose was measured for each condition, the resultant data is presented in Figure 6.10.

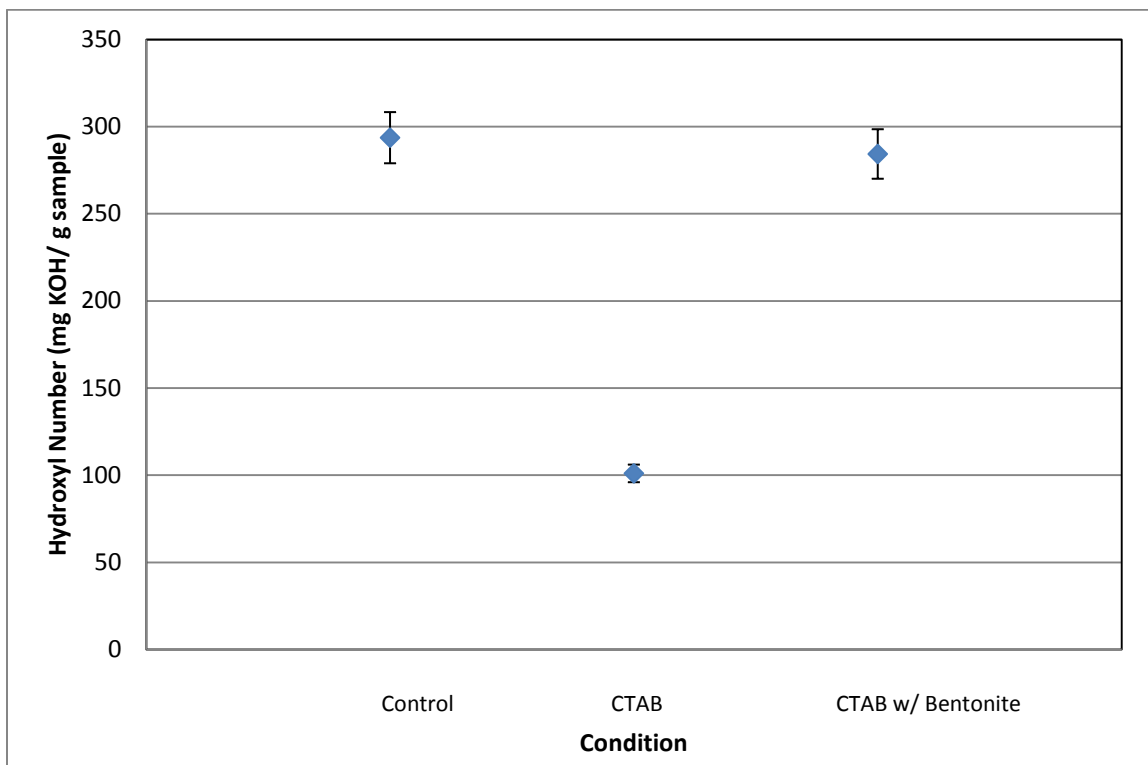


Figure 6.10. Hydroxyl number of a control condition, the addition of 1wt% CTAB, and subsequent addition of 4wt% bentonite.

Investigation of Figure 6.10 reveals that the number of hydroxyl sites of cellulose decreased from ~300 for the control to ~100 for 1 wt% addition of CTAB. This finding indicates that CTAB occupies hydroxyl sites on or within the fiber, and is consistent with the charge reversal of the system from an anionic state in the control to a cationic state in the presence of CTAB (Figure 6.9). The addition of bentonite recovers the hydroxyl number to that of the control condition, consequently proving CTAB removal from on or within the fiber via scavenging. The scavenging of the CTAB by bentonite must result in the formation of a

CTAB/bentonite complex which Figure 6.7 demonstrates is retained in the sheet. The retained CTAB/bentonite complex affects formation by opening up the sheet relative to the control sheet (lower KFI) as demonstrated by the data of Figure 6.7 and allows enhanced water removal. It is noted that in many ways the microparticle/CTAB addition mimics the successful formation/drainage/retention systems employed in the papermaking industry. Interestingly the data of Figure 6.4 indicates that the positive shift in pore size is not lost upon sequential addition of bentonite to a CTAB treated slurry, which correlates with the formation data of Figure 6.8. Therefore, it is concluded that the enhanced water removal mechanism seen with the post addition of bentonite to a CTAB treated pulp is due to a shift in pore size to larger diameters, whereas the enhanced water removal mechanism when only CTAB is present is attributed to a shift in pore size to larger pores, as well as an increase in the total pore volume.

An identical path of experimentation to that outlined for bentonite was also completed utilizing an alternative anionic scavenging molecule, anionic polyacrylamide (PAM). While similar trends to that of bentonite were observed, overall results with the addition of PAM lacked statistical consistency and hence are not presented.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The present work has developed and characterized a novel approach to the dewatering of a cellulose fiber mat. A significant void in the literature, and subsequent opportunity, were identified; specifically, the potential to apply chemical means to enhance water removal. The data of Chapter 4 demonstrates that the addition of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, to a pulp slurry significantly decreases the amount of water retained in the pulp after drainage and pressing (examined by the water retention value test (WRV)). Drainage was progressively increased with increasing dosage of CTAB up to a plateau at a dosage level of 1wt% on a dry fiber basis. The effectiveness of CTAB was demonstrated for pulps comprising a wide range of fiber types employed in papermaking in the Northeastern United States. Employing the relationship between WRV and the solids exiting the press section of a paper machine developed by Busker (1984), the CTAB WRV results suggest a potential 4% improvement in press solids. A mass balance around a hypothetical paper machine indicates that the 4% press solids correlates with a 16% increase in production rate. In order to evaluate if the effect observed with CTAB was attributable solely to the cationic surfactant, a slew of additives were screened with WRV testing. While some additives demonstrated a performance enhancement in dewatering, none approached the effectiveness of CTAB. The screening work demonstrated that the

reduction in surface tension induced by surfactant addition was partially, but not wholly, responsible for the reduction in the WRV. Given that water removed in the forming and pressing operations is governed by flow through a porous medium (cellulose fiber mat) attention was turned to parameters affecting removal of water from capillaries. Specifically, investigation of the Young-Laplace equation led to examination of the effect of CTAB on the contact angle of water at the solid/liquid interface. Measurements within capillaries demonstrated that the addition of CTAB significantly increased the contact angle, which in turn decreased the water column height, a finding that would improve water removal in a fibrous mat. Evaluation of the solution concentration of CTAB revealed that vast majority of the surfactant was resident either at the air/water interface, or on or within the fibers. Measurement of the streaming potential and total charge of a CTAB dosed pulp slurry revealed that CTAB was adsorbed on the cellulose fiber via observation that the previously anionic fiber system was charged reversed to a cationic system.

Visual observations of WRV pads and handsheets made from CTAB dosed pulps revealed that they were significantly thicker relative to controls. An examination of the pore structure of the WRV pads was therefore undertaken. Mercury porosimetry revealed that with the addition of CTAB, the pore structure of the fiber mat shifted to larger pore radii with a concomitant increase in the number of pores. The Young-Laplace equation indicates pore radius has an inverse relationship with capillary pressure. As such, the increase in pore radii observed in the presence of CTAB results in an enhanced rate of water removal due to a reduction in the force holding water within fiber capillaries. The strength of CTAB

dosed sheets was found to be significantly decreased relative to control sheets; a fact at least partially attributable to decreased fiber-fiber hydrogen bonding arising from the bulking. In addition, determination of the number of available surface hydroxyl groups on fibers revealed that in the presence of CTAB approximately 60% of the groups were masked by the surfactant. This effect would be expected to decrease the extent of fiber-fiber hydrogen bonding, thereby contributing to the loss of sheet strength.

In order to determine if the laboratory observations could be scaled up, two pilot trials were undertaken to examine the performance of the technology on the machine scale. The University of Maine's Process Development Center (PDC) pilot testing facilities for papermaking process research and development were employed for this purpose. The first trial demonstrated that the addition of CTAB to a pulp slurry enhanced water removal in the paper making process. Indeed all trends observed in the laboratory study (Chapter 4) were successfully scaled to the pilot machine. Enhanced water removal was demonstrated in both forming and pressing sections, the headbox charge was decreased, as was the bond strength of the sheet. In addition, the bulking and change in pore structure observed on the bench scale was replicated on the pilot scale.

The second pilot scale machine trial was designed and implemented to examine two separate aspects of chemically enhanced water removal, scale up of the dual addition of CTAB and the Telioform system; and optimization of the addition points of CTAB when used as the sole additive. Critically, the trial was configured to quantify enhanced dewatering through quantification of the production rate

increases via running the machine in a dryer limited state and manipulating speed whilst maintaining reel solids. If enhanced dewatering occurred in the forming and/or pressing section the water load into the dryer section would decrease and machine speed could be increased to reinstate a dryer limited scenario, correlating with an increase in production. Data from the second machine trial supported the laboratory based findings that the addition of CTAB to a pulp slurry significantly improves water removal in the paper making process. Indeed the most favorable trial condition resulted in a production increase of 18%, with the measured press solids suggesting a further 12% production increase may have been achievable. These realized and unrealized production gains easily allow the technology to be economically viable. It is noted however, that the technology results in a significant loss of sheet strength. It is likely that CTAB resident on the fiber surface inhibits fiber-fiber hydrogen bonding required for sheet strength. In addition, electrostatic repulsion of fibers due to reversal of the charge of the system by CTAB results in bulking of the sheet and further inhibits fiber-fiber bonding. The resultant changes in fiber distribution within the sheet creates an increased pore volume and a shift to larger pore sizes in the presence of CTAB, leading to enhanced dewatering. As may be expected however, the formation of the sheet is negatively impacted by the addition of CTAB.

Mutek system charge, ATR-IR measurement of solution concentration, and surface tension data suggest that a greater quantity of CTAB is located on or within the fiber when the surfactant is added in the disintegration step of slurry preparation, as opposed to addition during refining or at the machine chest. As such

the most favorable addition for CTAB was observed during disintegration. These results mirror those acquired in bench top experimentation and therefore represent a successful translation of the technology to the pilot scale. It is noted however that attempts to employ CTAB in conjunction with a commonly used formation, drainage, and retention system (Telioform) were largely unsuccessful, and did not demonstrate improvements seen on the bench scale. Examination of tray solids in the Telioform conditions led to the conclusion that upon CTAB addition to the system the retention chemistry was disrupted (tray solids increased in the presence of CTAB illustrating a loss of retention). It was hypothesized that the shorter residence times on the pilot machine, in comparison to the bench scale, CTAB competed with the cationic component of the Telioform system in combining with bentonite; leading to a hindering of both mechanisms.

The loss of sheet strength is a result that many manufactures would find unacceptable since many grades of paper, and paper products, are sold on a strength basis. In addition, the observed decrease in surface tension and increase in sheet bulk are potential barriers to the technology's implementation in a production environment. In order to mitigate these negative effects, an anionic scavenger (bentonite clay) was employed to attempt to remove CTAB resident on the exterior of the fiber surfaces to determine if the surfactant was giving rise to bulking and decreasing fiber-fiber hydrogen bonding. Indeed, the addition of bentonite yielded a recovery of the surface tension, streaming potential and total charge, and a reduction in bulking, whilst maintaining a reduction in the WRV. However, sheet strength was not recovered to a level that would be deemed acceptable by the

industry. The scavenging of the CTAB by bentonite results in the formation of a CTAB/bentonite complex which is retained in the sheet. The retained CTAB/bentonite complex affects formation by opening up the sheet in relation to the control (lower KFI) and allows enhanced water removal. Therefore, it is concluded that the enhanced water removal mechanism seen with the post addition of bentonite to a CTAB treated pulp is due to a shift in pore size to larger values, whereas the enhanced water removal mechanism when only CTAB is present is attributed to a shift in pore size to larger pores, as well as an increase in total pore volume.

7.2 Recommendations

The technology developed in the present work likely has a niche application within the pulp and paper industry. Direct application of the addition of CTAB to a system to enhance water removal may be employed in situations where machines are dryer or press limited, and the loss of formation and sheet strength are non-factors in measurement of product quality. For paper grades where formation and sheet strength are critical aspects of the paper product, additional work must be performed in order to optimize the additive, or its mode of addition, to reduce the negative impacts while maintaining gains in water removal. Further examination of the two component addition should be explored with an emphasis on manipulating known parameters to increase strength and to improve formation such as refining, and the jet-to-wire ratio. It may also be possible to introduce a low cost strength additive to the wet end to recover sheet strength and truly develop a multi-

component system. More generally the present work demonstrates that a wet end cationic additive may be employed with comparative ease to manipulate the pore structure of a sheet, opening up a host of possibilities.

REFERENCES

- Abson D, Gilbert R D (1980) Observations on water retention values. Tappi 63(9):146-147
- Alila S, Boufi S, Belgacem M N, Beneventi (2005) Adsorption of a cationic surfactant onto cellulosic fibers I. surface charge effects. Langmuir 21:8106-8113
- Alila S, Aloulou F, Beneventi, Boufi S (2007) Self-aggregation of cationic surfactants onto oxidized cellulose fibers and coadsorption of organic compounds. Langmuir 23:3723-3731
- Aloulou F, Boufi S, Belgacem N, Gandini A (2004) Adsorption of cationic surfactants and subsequent adsolubilization of organic compounds onto cellulose fibers. Colloid Polym Sci 283:344-350
- Anderson L, Back E (1981) The effect of temperature up to 90 deg C on dewatering of wet paper webs, evaluated in a press simulator. Proceedings Tappi Engineering Conference 311-323
- Bliesner W C (1978) Sheet water removal in a press: time to review the fundamentals. Pulp and Pap 52:75-77
- Backstrom M, Drotz M, Tubek-Lindblom A, Blohm E (2009) Improved product quality and increased production capacity with impulse technology. Pulp and Pap Canada 110:33-36
- Busker L H (1980) Wet press water removal over a wide parameter range. Pap Tech and Ind 21:91-96/109
- Busker L H, Cronin D C (1984) The relative importance of wet press variables in water removal. Pulp and Pap Can 85:87-101
- Butterfield B G, Meylan B A (1980) Three-dimensional structure of wood an ultrastructural approach. 2nd edn. Chapman and Hall, London
- Campbell W B (1947) The physics of water removal. Pulp and Pap Mag of Canada Convention Issue:103-122
- Ceckler W H, Thompson E V (1982) The university of maine at orono wet pressing project. University of Maine at Orono, Orono

- Caulfield D F, Young T L, Wegner T H (1982) The role of web properties in water removal by wet pressing. Tappi 65:65-69
- Caulfield D F, Young T L, Wegner T H (1986) How web and press parameters interact to control water removal in the wet press. Tappi J 69:90-93
- Cole B J W (2009) Wood chemistry: a course in wood and biomaterial chemistry, course notes. University of Maine, Orono
- Côté Jr W A (1967) Wood ultrastructure. University of Washington Press, Syracuse
- Gullichsen J, Fogelholm C J (1999) Paper science and technology: chemical pulping. Fapet Oy, Helsinki
- Harrick N J (1967) Internal reflection spectroscopy. Interscience Publishers, New York, NY
- Jayme G (1958) Properties of wood celluloses II determination and significance of water retention values. Tappi 41(11):180A-183A
- Lobosco V (2004) On the modeling of mechanical dewatering in papermaking. Dissertation Royal Institute of Technology, Stockholm, Sweden
- Lucisano M F C, Petrini J B, Martin A R (2003) The role of evaporative dewatering in impulse drying. Tappi J 2(3):26-32
- MacGregor M A (1998) Wet pressing and paper properties – a micromechanical view. STFI Proceedings February 1998. Stockholm, Sweden
- Moore W J (1972) Physical chemistry. 5th edn. Prentice-Hall Inc, Englewood Cliffs
- Neivandt D J (1998) Co-adsorption of polyelectrolytes and surfactants at the silica/solution interface. Dissertation University of Melbourne, Australia
- Park S, Venditti R A, Jameel H, Pawlak J J (2007) Hard-to-remove water in cellulose fibers characterized by high resolution thermogravimetric analysis. Tappi J 6(7):10-16
- Park S, Venditti R A, Jameel H, Pawlak J J (2006) Hard to remove water in cellulose fibers characterized by high resolution thermogravimetric analysis. - methods development. Cellulose 13:23-30

- Paulapuro H, Gullichsen J (2000) Papermaking part 1, stock preparation and wet end. Papermaking Science and Technology. Finnish Paper Engineers' Association and TAPPI, Helsinki, Finland
- Robertson G J (1976) The evaluation and improvement of press section performance, some practical aspects. *Appita* 30:62-67
- Ruthven D (1984) Principles of adsorption and adsorption processes. J Wiley and Sons, New York
- Scott W E (1996) Principles of Wet End Chemistry, TAPPI Press, Atlanta, GA
- Sjostrom E (1993) Wood chemistry: fundamentals and applications. 2nd edn. Academic Press, San Diego
- Smart F R (1975) Water removal performance on a grooved second press, part 1. *Pap Tech and Ind* 16:172-178
- Smook G (2002) Handbook for pulp and paper technologists. 3rd edn. Angus Wilde Publications Inc, Vancouver
- Springer A, Nabors L A, Bhatia O (1991) The influence of fiber, sheet structural properties, and chemical additives on wet pressing. *Tappi J* 4(2):221-228
- Stratton R A (1982) Use of polymers in wet pressing. *Tappi Proceedings Papermakers Conference* 179-185
- Tappi Useful Method 256: Water retention value
- Thode E F, Bergomi Jr J G, Unson R E (1960) The application of a centrifugal water-retention test to pulp evaluation. *Tappi* 43(5):505-512
- Thorne J T (1981) The effect of capillary rewet on wet pressing operations. Dissertation University of Maine at Orono
- Tze W T, Gardner D J (2001) Contact angle and IGC measurements for probing surface-chemical changes in the recycling of wood pulp fibers. *J Adhesion Sci Technology* 15(2):223-241
- Wahlstrom B P (1960) A long term study of water removal and moisture distribution on a newsprint machine press section: part 1. *Pulp and Pap Mag of Canada* 61:380-401

Wahlstrom B P (1969) Our present understanding of the fundamentals of pressing. Pulp and Pap Mag Canada 70:349-369

Wahlstrom B P (1981) Opportunities in pressing: part 1. Tappi 64:75-78

Wahlstrom B P (1991) Pressing – the state of the art and future possibilities. Pap Tech 18:227-236

Wahlstrom B P (2001) Wet pressing in the 20th century: evolution, understanding and future. Pulp and Pap Canada 102:81-88

Wegner T H (1987) The effect of polymeric additive on papermaking. Tappi J 7:107-111

Wistara N, Young R A (1999) Properties and treatments of pulps from recycled paper. part I. physical and chemical properties of pulps. Cellulose 6:291-324

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