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SUPERCRITICAL CARBON DIOXIDE DEINKING AND DEWAXING

by

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SUPERCRITICAL CARBON DIXOIDE DEINKING AND DEWAXING

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Western Michigan University, 2007

The main purpose of this project is to study how the supercritical carbon dioxide ($ScCO_2$) fluid can be used to extract sticky compounds and commercial printing inks. This study will focus on the upscale unit operation that Western Michigan University had recently installed supercritical fluid extraction system. This also includes determination of extraction efficiency, optimizing operating condition, the effect of $ScCO_2$ on the fiber tensile strength for recycling paper after the sticky compounds are removed and the effect of $ScCO_2$ to the fiber physical strength property at different temperatures.

The investigation of supercritical fluid extraction equipment on sticky compounds demonstrated that the equipment is able to extract sticky compounds; such as paraffin wax, hot-melt adhesive and PVAc. The equipment delivered high extraction efficiency on paraffin wax by utilizing a continuous process. The results show that extraction efficiency is dependent on the temperature and pressure. For printing inks, the extraction is not able to extract and remove ink particles from inside the reactor. $ScCO_2$ fluid has no effect to fiber physical strength at temperature ≤80°C, 5000 psia. At 105°C, the fibers showed a reduction in fiber strength from the zero-span breaking strength test. Tensile index and internal bond strength tests showed no significant reduction in fiber bonding strength.

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CHAPTER I

INTRODUCTION

Overall Technology Description

The deinking process for recycling post consumer waste has become an increasing challenge to remove ink and sticky compounds from the recovered paper as many new printing processes, new kinds of ink, and newly formulated glues and binders have been invented over the years. It is difficult or impossible to remove all kinds of ink and impurities. First, the waste papers are sorted. Not all paper can be recycled. Papers that are waxed, coated with plastic or aluminum foil are not recyclable and rejected, but not all are removed. Therefore, a deinking process is designed to produce recycled fiber pulp with high whiteness and purity. Currently, the methods of removing ink and impurities are done by washing, flotation, and dispersing.

Carbon dioxide (CO_2) is environmentally friendly, nontoxic, non flammable and inexpensive. CO_2 is the most common solvent used in supercritical fluid extraction. It has a critical temperature of 31.1°C and critical pressure 7.38 MPa, which is easy to achieve. Supercritical (Sc) fluids can have solvating powers similar to organic solvents, but with higher diffusivities and lower viscosity. The solvating power can be adjusted by changing the pressure or temperature, or by adding modifiers or co-solvents to the supercritical fluid [1]. Several experiments have been reported and patented of using supercritical carbon dioxide to remove wax and sticky compounds from old corrugated containers [2, 3].

Most of the contaminants and sticky compounds are soluble in a number of organic solvents. The problems raised by using organic solvents are the cost and environmental pressure. Supercritical fluid extraction has brought more interest in paper recycling. Supercritical fluids have many features that are suitable for process control. The density of supercritical fluids, which is an important factor of solubility, is sensitive to temperature and pressure. This is a suitable property for process control [4, 5].

In this study, the supercritical carbon dioxide ($ScCO_2$) will be used to extract sticky compounds and ink contaminants from the fiber substrate. The efficiency of the $ScCO_2$ extraction will be determined by the amount of contaminates removed and any changes in physical strength of the fibers. Printing inks are made up of color pigments, ink vehicle/organic solvents, binders and additives. $ScCO_2$ will be used to extract and find possibilities to move the ink and its components.

CHAPTER II

LITERATURE REVIEW

Overview of Deinking Operations

In the deinking mill, the recovered paper has to undergo several unit operations in order to remove contaminants. The contaminants include inks, adhesives and glues, rosin, waxes, starches and gums, coatings, paper fillers, polystyrene foam, and plastics from bags and tape. Adhesives, glues, and waxes fall into the category called "stickies". The unit operations to remove these contaminants are washing, flotation, cleaning, and screening. The different stages are designed to remove a particular particle size to obtain the maximum efficiency of contaminant removal.

First, the recovered paper has to undergo pulping by mechanical and chemical action to promote ink detachment from cellulose fibers. Mechanical action is fiber to fiber abrasion and fiber flexing and bending. Chemical action includes swelling of fibers, emulsification of ink particles by the surfactant, and solubilization. The surfactants are added to promote ink particle detachment from fibers and dispersion of detached ink in the process water. It also controls the particle size of ink particles detached from cellulose fibers during pulping.

The pulp slurries then go through high density cleaning and screening [6]. The high and medium density large particles such as rocks and dirt, nuts, bolts, nails, paper clips, and other objects are removed. The centrifugal forces separate the less dense cellulose fibers from the heavier objects. Screening is also used to remove large ink particles and low-density contaminants.

After screening is the washing stage, where the dispersed ink particles are removed from pulp slurries. Washing is most effective in removing small, dispersed ink particles, such as from letterpress, offset, and aqueous flexographic newsprint inks.

The flotation process is done by blowing air bubbles through the bottom of the flotation cell [7]. The ink particles, filler, and coating particles are attached to air bubbles. The surfactants adsorbed on ink particles render them hydrophobic to promote adsorption onto air bubbles. The adsorbed ink, filler, and coating particles rise with the bubbles to the top of the flotation cell. The foam layer traps these solids and removes them. In the actual process, all of the contaminants are not 100% removed and remain in the pulp slurry. The remaining ink particles and sticky can deposit on the forming fabrics, press felts and dryers of the paper machine. Sticky compounds in recycled paper fibers reduce paper quality and strength. Reduced in fiber bonding strengths (paper tensile property) can cause web breaks and paper machine down time. The recycled paper products are not made from 100% recycle pulp. Paper cannot be recycled repeatedly. Eventually the fibers become too weak and short to be used again. Virgin paper fiber is usually mixed with recycled fiber to increase paper physical strength.

Overview of Supercritical Fluid Extraction and Its Properties

A supercritical fluid is a substance above its critical pressure and critical temperature. Above this critical point, the substance cannot be condensed or evaporated to form a liquid or a gas, but is a fluid. The fluid is considered to have both gas-like and liquid-like properties. This gives an advantage to supercritical fluid extraction over conventional solvent extraction.

Carbon dioxide (CO_2) is by far the most widely used gas for supercritical fluid extraction. It has a convenient critical temperature, non-explosive character, and non-toxicity. Table 1 shows the critical properties of various solvents. The other advantages of using CO_2 are that it is cheap and abundant, the solvent is easily removed, and pressure and temperature can easily change its density and selectivity of the extraction. Other solvents listed in Table 1 can easily achieve their critical points, but they are very toxic if used at high concentration.

Table 1: Critical properties of various solvents (Reid et al, 1987) [8]

Solvent	**Molecular Weight**	**Temperature**	**Pressure**		**Density**
	(g/mol)	(K)	(MPa)	(bar)	(g/cm^3)
Carbon Dioxide	44.01	304.1	7.38	73.8	0.469
Water	18.02	647.3	22.12	221.2	0.348
Methane	16.04	190.4	4.60	46.0	0.162
Ethane	30.07	305.3	4.87	48.0	0.203
Propane	44.09	369.8	4.25	42.5	0.217
Ethylene	28.05	282.4	5.04	50.4	0.215
Propylene	42.08	364.9	4.60	46.0	0.232
Methanol	32.04	512.6	8.09	80.9	0.272
Ethanol	46.07	513.9	6.14	61.4	0.276
Acetone	58.08	508.1	4.70	47.0	0.278

Figure 1 shows the density-pressure isotherms for carbon dioxide. The density change is seen to increase rapidly at around the critical pressure, because the compressibility diverges at the critical point. As the temperature is raised the change is less dramatic with move to higher pressures. This makes supercritical CO_2 more difficult to control around the critical pressure. On the other hand, this gives a wider range of the fluid density for the extraction process to be controlled. This also gives the soluble compound to be selected, because different compounds are soluble at different supercritical fluid densities.

Table 2 shows the properties, density (ρ), viscosity (η), and diffusion coefficient (D) for naphthalene in CO_2, and of CO_2 in various phases. The supercritical phase of CO_2 has high density, low viscosity, and a high diffusion coefficient. This gives the supercritical CO_2 behavior of a soluble liquid and better transport/diffusion into pores of solid compounds as the gas-like property in the extraction.

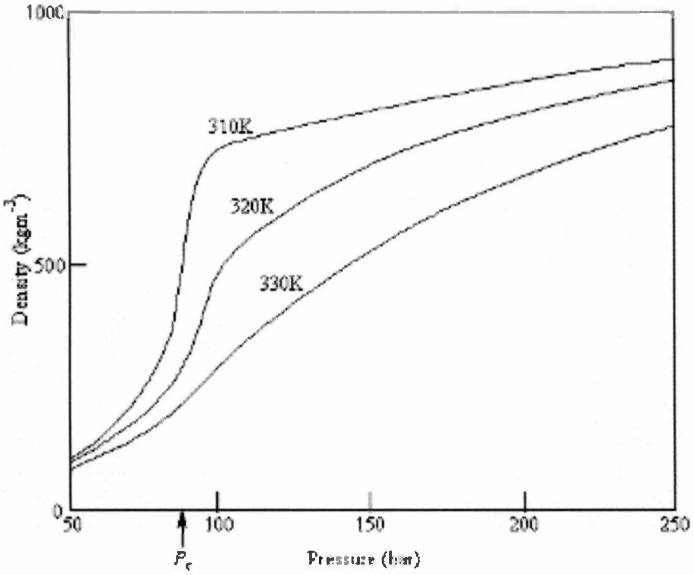

Figure 1: Density-pressure isotherms for carbon dioxide [9]

Table 2: The density (ρ), viscosity (η), and diffusion coefficient (D) for naphthalene in various phases of CO_2 [10]

Phase	ρ (kg m^{-3})	η (μPa s)	*D* (m^2 s^{-1})
Gas (313K, 1 bar)	2	16	5.1×10^{-6}
Supercritical (313 K, 100 bar)	632	17	1.4×10^{-8}
Liquid (300 K, 500 bar)	1029	133	8.7×10^{-9}

CO_2 is a poor solvent for high molecular weight or hydrophilic molecules, because of its very low dielectric constant and nonpolar nature, which limits wider application. Small amounts of polar-solvents can enhance the solubility of a polar solute in $ScCO_2$. The co-solvents enhance the solubility significantly near the critical region [11]. The polar co-solvent increases the interaction with the solute by increasing the local density around it or "clustering". Clustering is defined as a situation in which the local density within the bulk around the solute is larger than the average density of the fluid. Another consideration when using the supercritical CO_2 is the presence of water. Water is not soluble in supercritical CO_2. It can form a mask around the compound that is to be extracted. This will interfere with the rate of extraction. It is recommended the sample to be tested should be dried as much as possible.

Overview of Paper Physical Properties

When paper is made, pulp fibers are dispersed in water and drained through the forming fabric, which separates the pulps and water to form a layer of pulp. The layer of pulp is pressed to remove excess water and sent to the dryer unit to evaporate hard to remove water and maintain proper paper moisture content. Several physical properties of paper can be tested to determine the strength of the paper and the pulp that it is made of. Basic tests such as tensile strength, internal bond strength and zero-span tensile tests are used as a standard to determine physical strength and quality of paper.

Tensile strength is defined as the maximum tensile force developed in a test specimen before rupture [12]. Tensile strength is the force per unit width of test specimen. Papers are made of fibers bonding together. On a paper machine, paper tensile strength is very important to maintain the paper web from breaking. Faster machine speed will produce high stress on the web, which requires paper to have higher tensile strength. Paper tensile strength can be derived from many factors; such as fiber strength, fiber length, and bonding. Tensile index can be measured by using TAPPI T-494 standard. The calculation is using the equation:

$$TI = 1000\left(\frac{T}{R}\right)$$

Where, TI is tensile index [N*m/g], T is tensile strength [kN/m] and R is grammage (dry air) [g/m^2].

Tensile index measures the strength of paper in the "x" and "y" plane of paper or machine-direction or cross-direction of the paper. Internal bonding strength (Scott type) measures the bonding strength of fibers in the z-direction tensile by using TAPPI T-569 standard method. This test method tests the energy per unit area [ft. lbs. x 10^{-3} / in^2] required to rupture and split the paper.

Zero-span breaking strength of pulp is a quick way to determine the tensile strength for a random oriented specimen of fibers. This method is commonly used to check the fiber quality and comparison between different types of fibers. TAPPI T-231 standard method is commonly used to determine the strength of fibers, not bonding strength of fibers in the paper as defined in tensile index and internal bonding strength measurements. In doing so, the measurement results will measure the strength of fiber per unit length [N/cm].

CHAPTER III

PROBLEM STATEMENT

WMU has installed the supercritical fluid extraction system from Supercritical Fluid Technologies, Inc. The equipment is able to operate up to 10,000 psi (68.9 MPa) pressure and up to 200°C (473 K) in temperature. The system is able to compress CO_2 gas and raise its temperature to achieved supercritical fluid condition. $ScCO_2$ fluid can be used to extract a specific compound from inside the reactor. Co-solvent can be externally pumped into the system to increase the solubility power of the $ScCO_2$ fluid.

The main purpose of this project is to study how the equipment can be used to extract sticky compounds and commercial printing inks. This is a continuation of previous research conducted at WMU [13]. This new study focuses on the upscale unit operation. This will also include determination of extraction efficiency, optimizing operating condition, the effect of $ScCO_2$ on the fibers tensile strength property for recycling paper after the sticky compounds are removed and the effect of $ScCO_2$ on the fiber physical strength property at different temperatures. The experimental work can be broken down into four sections.

The first section is determining optimal operating condition for extracting sticky compounds that are widely used in the industry, such as paraffin wax, hot-melt and polyvinyl acetate (PVAc). Co-solvents will also be used to find possible increases in extraction efficiency. The second section is to determine the extraction efficiency for extracting commercial printing inks. Commercial printing inks contain ink vehicle or solvent, which help the ink to flow and print onto the substrate. The solvent will eventually evaporate as the ink dries. Determining the percentage of ink that evaporates will be done in the oven and will be compared to the percentage of ink that can be extracted by utilizing $ScCO_2$. The third section is to determine the effect of $ScCO_2$ on the fiber tensile strength property and removal of paraffin wax from wax coated bleached softwood handsheet. The first three sections will use a 100 mL extraction vessel. The last section, in addition to the third section, utilizes a 2 L extraction vessel for extraction on pure fiber handsheet at three different temperatures and a study of the effect of $ScCO_2$ on fiber physical strength properties.

CHAPTER IV

EXPERIMENTAL

Materials and Equipments Used

Printing Inks

- Sheet-fed litho offset ink
- Gravure toluene based ink

Equipment

- Weight scale
- Aluminum foil
- 30 ml septum glass vial
- SFT-150 SFE/SFR system
    - 100 ml & 2 L extraction vessels
    - Co-solvent pump added ability
    - Maximum pressure: 10,000 psia (68.9 mPa)
    - Temperature range: Ambient to 200ºC

Solvents

- Dichloromethane (HPLC grade)

Sticky compounds

- Paraffin Wax
- Hot-melt adhesive
- Polyvinyl acetate (PVAc)

Fiber type

- Bleached softwood pulp

Design of Experiment

Supercritical Fluid Extraction System

The Equipment SFT-150 is used and the experimental setup is shown in Figure 2. The system consists of a cylinder tank with siphon for supplying liquid CO_2. The chiller maintains the temperature at 5°C to prevent the liquid CO_2 from expanding into a gas prior feeding to piston pump. Liquid CO_2 is then expanding into the gaseous state, as the temperature increases at the preheater. The reaction vessel can hold 100 mL in volume. The vessel itself has a heating jacket around it, which increases the temperature of the CO_2 to the desired temperature.

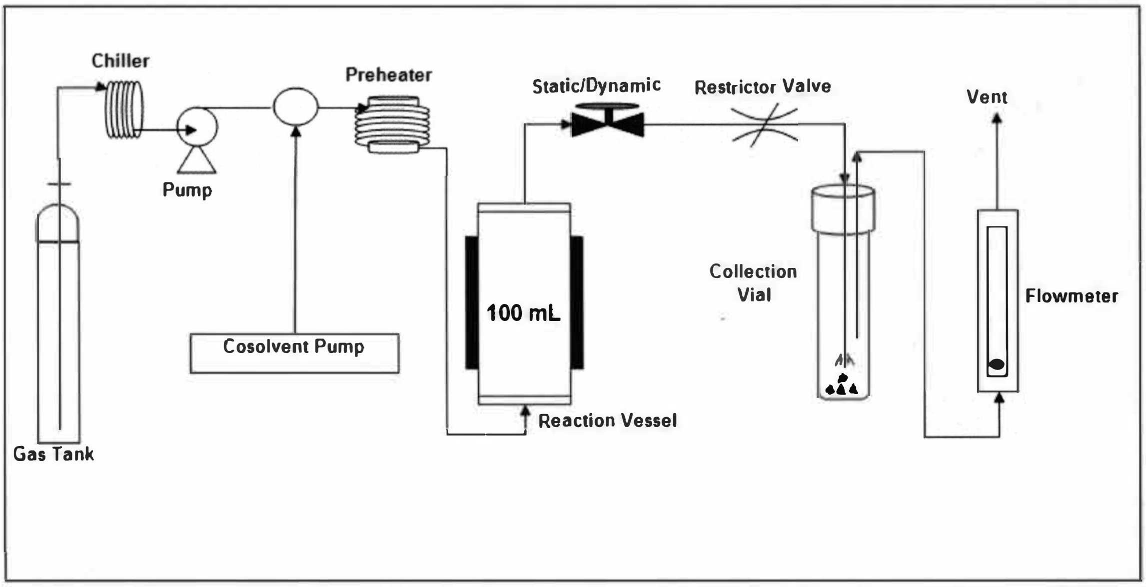

Figure 2: Experimental Setup for Supercritical CO_2 Extraction

As the pressure and temperature are high enough to achieve $ScCO_2$ fluid, the sample, which is initially put inside the reactor, will be dissolved in the fluid. The fluid is transferred through static/dynamic value or on/off value and restrictor valve. The restrictor valve will control the flow rate of extraction. The decompression will happen after the restrictor valve, at which time the fluid turns back into the gaseous state and dissolved compounds deposit back into their original physical state and collect into the collection vial creating 100% separation. The CO_2 gas will vent through a transfer line to the flowmeter that monitors the system extraction rate. The co-solvent can be added to the system by the external co-solvent pump to enhance the extraction efficiency.

Methodology

The design of experiments was separated into four parts. The first three parts utilized the 100 ml extraction vessel. In the first part, the experiments were conducted to study how the equipment behaves in batch and continuous processes at different temperatures and pressures, at which small amounts of paraffin wax were extracted. This was to determine the extraction efficiency for the paraffin wax by weighing the sample before and after the extraction. In the batch process, the sample was left inside the reactor for one hour before opening the valve to start the collection. In the continuous process, the pressure was maintained constant throughout the collection for three hours, while new collection vials were constantly changed at 15th, 30th, 45th, 60th, 90th, 120th, 150th and 180th minutes. This was to determine how long is required to conduct a continuous extraction experiment and for extracting hot-melt adhesive and PVAc. The co-solvent was added to the system at five percent by vessel volume and the results compared. The co-solvent used was dichloromethane (CH_2Cl_2). Dichloromethane has a similar dipole moment value to methanol and ethanol [14]. Methanol and ethanol are commonly used as additive co-solvents in $ScCO_2$ extraction process. Methanol and ethanol have boiling points of 68 and 78°C respectively, which are higher than the boiling point of dichloromethane, 40°C. During sample collection using the septum vial, if methanol or ethanol were used, the weight of the sample collected would contain the sticky compound and a small amount of co-solvent. The additional weight of co-solvent in the sticky compound would be undetermined by weight and take time to evaporate. Using dichloromethane, which has a lower boiling point and high evaporation rate, will not affect the weight of sticky compound collected.

The second part of the research was to determine if the $ScCO_2$ fluid extraction is capable in extracting/deinking commercial printing inks. Gravure toluene cyan ink and black offset ink were used for this. The results were to compare how much solvent or liquid does the ink contain and evaporate after the ink is dry. The ink samples were dried inside the oven overnight.

The third part of the research was to determine of the effect of $ScCO_2$ on the fiber tensile strength property after recycling and the efficiency of paraffin wax removal from wax coated handsheet. The handsheets were made from bleached softwood pulp by TAPPI T-205 and T-227 procedures. The finished handsheets were stored in the control environment room at 50% RH and 23°C to keep the moisture content relatively the same for every handsheet.

The paraffin wax coating was applied by first melting the wax using the crucible on the hotplate. The hotplate was covered with the aluminum foil to avoid wax sticking and burning on the heating surface. Then, the weighted handsheet was put on the hotplate and was coated with the melted hot wax. A doctor blade was used to coat the wax evenly on one side of the handsheet. The handsheet was removed from the hotplate to cool.

The coated wax handsheet was torn into half and then quarters before tearing into long strips about one centimeter wide. The coated wax handsheet was weighed before and after the extraction to determine the weight lost and extraction efficiency of $ScCO_2$. The extracted handsheets were repulped and remade into handsheets by using the TAPPI T-205 procedure. The individual handsheet was repulped for one minute in the disintegrator until all fiber bundles were dispersed, simulating the recycling process.

The finished recycled handsheets were tested for their tensile strength according to the TAPPI T-494 method. Table 3 shows the experimental conditions for the wax-coated handsheets. Group 1 represents the control group where the handsheets were recycled, but never treated with wax and $ScCO_2$ extraction. Group 2 to 5, the handsheets were treated with $ScCO_2$ extraction, but Group 5 represents pure fibers without any wax coated. In Group 6, the handsheets were oven heated at 50°C to simulate the same amount of heating effect that occurs in the $ScCO_2$ reactor, similar to Group 5, but at the atmospheric pressure.

Table 3: Experimental Condition for Paraffin Wax Coated Handsheets

Group	Wax Coated	$ScCO_2$ Extraction	Pressure (psia)	Temp. (°C)
1	No	No	-	-
2	Yes	Yes	5000	50
3	Yes	Yes	5000	40
4	Yes	Yes	4000	50
5	No	Yes	5000	50
6	No	No	14.69	50

The last part of the research was to determine the effect of fiber strength after treating with $ScCO_2$. These experiments utilized the 2 L extraction vessel. A new batch of pulps was used to make new 68 handsheets for the last part of the research and evenly divided into four groups, 17 handsheets each. 17 handsheets were put inside the vessel for each run/experimental group. Table 4 shows the experimental conditions for each group. Group A represents the control, where no $ScCO_2$ treatment was done to the handsheets. Group B, C and D were treated with $ScCO_2$ at 50, 80 and 105°C respectively at 5000 psia pressure for two hours. After the extractions and no extraction for Group A, each group, all the handsheets were soaked overnight and redispersed together in the disintegrator for 5 minutes. The dispersed pulps were mixed with additional water to make up the consistency as stated in TAPPI T-205 before being made into handsheets for physical strength tests. The tests consisted of tensile, internal bonding strength and zero-span breaking strength tests by TAPPI test methods T-494, T-569 and T-231 respectively.

Table 4: Experimental Condition in 2 L Extraction Vessels for 2 Hours

Group	**$ScCO_2$ Extraction**	**Pressure (psia)**	**Temp. (°C)**
A	No	-	-
B	Yes	5000	50
C	Yes	5000	80
D	Yes	5000	105

CHAPTER V

RESULTS AND DISCUSSION

In the first part of the research, an experiment was conducted to study how the equipment behaves in batch and continuous processes at different pressures and temperatures. The experimental results for paraffin wax extraction are shown in Table 14. Table 5 and Figure 3 shows the summary data for the percentages of paraffin wax that were extracted in a batch process at 40°C and increasing pressures. The extraction efficiency for batch process initially increases with increasing pressure, but falls off somewhere after the pressure has exceeded 6000 psia.

Table 5: Percentage paraffin wax extracted at constant temperature and various pressure in a batch process

Temp (°C)	Pressure (psia)	% Extracted
40	4000	18.43
40	6000	37.19
40	7000	34.27

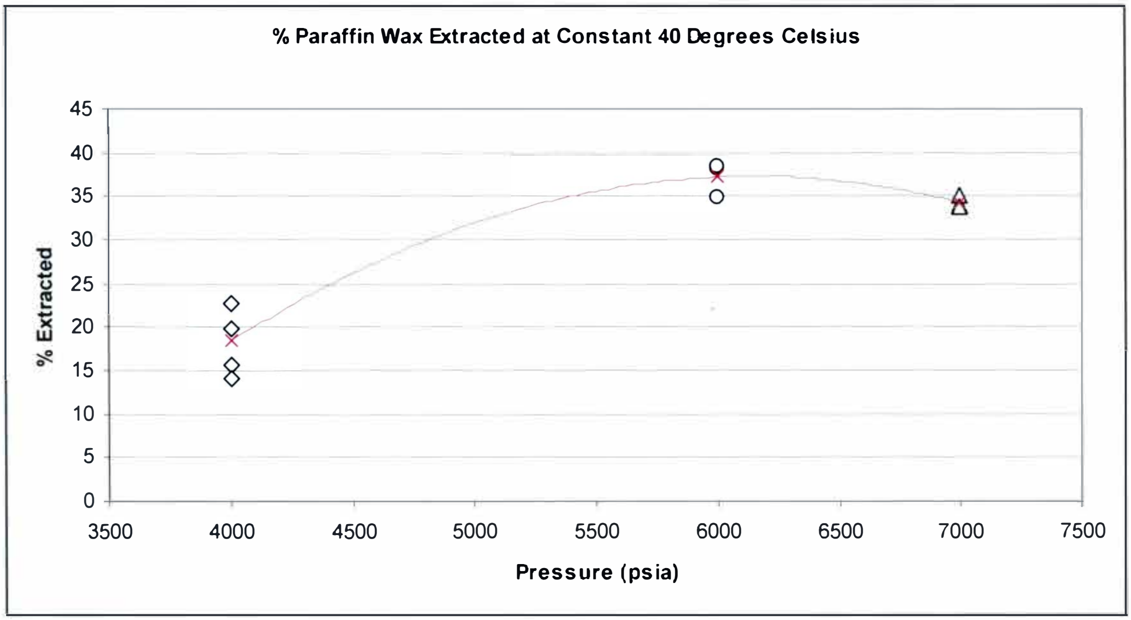

Figure 3: Correlation between percentage paraffin wax extracted and pressure at constant temperature

Table 6 and Figure 4 show the summary data for percentages of paraffin wax extracted with increasing temperature. During the experiment, as the temperature increases, the pressure could not be maintained constant at 4000 psia. Therefore, at temperatures higher than 70°C the experiments were conducted at 5000 psia. Figure 4 shows the extraction efficiency increasing with increasing in temperature.

Table 6: Percentages of paraffin wax extracted at increasing temperature in a batch process

Temp(°C)	Pressure (psia)	% Extracted
40	4000	18.43
55	4000	27.79
65	4000	32.30
75	5000	36.75
90	5000	48.25

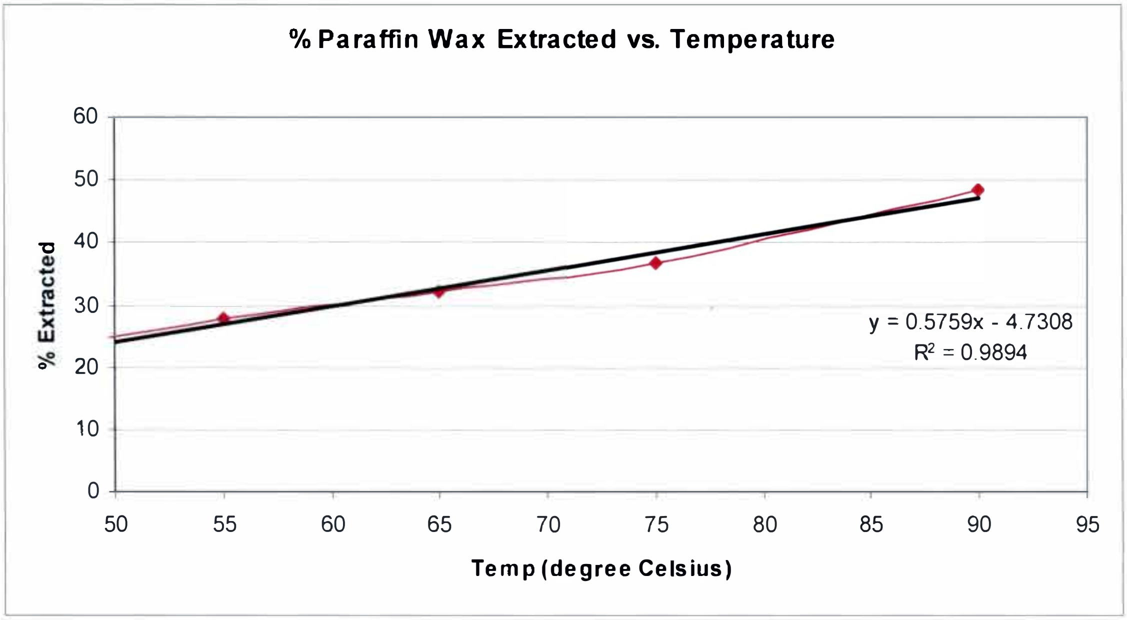

Figure 4: Correlation between percentage paraffin wax extracted and temperature

In the continuous extraction process, the pressure was maintained constant throughout the collection for three hours. At the same time, new collection vials were constantly changed at the 15th, 30th, 45th, 60th, 90th, 120th, 150th and 180th minutes. It was suspected that there would be some accumulations inside the piping system. Therefore, after three hours of extraction or during decompression, another collection vial was used to collect the remaining wax that came out. During the decompression, the $ScCO_2$ fluid turned back into gases state after the pressure inside the reactor went lower than its critical pressure. The reactor maintained the experimental temperature, which produced relatively warm gas that was hot enough to soften the wax and pushed it through the piping system and into the collection vial. This procedure was called "flush". Figure 5 shows the percentages of paraffin wax were extracted at different time intervals. During the first 45 minutes, the continuous process was able to extract ~74%. The figure also shows that during the flush, there was some small amount of wax stuck inside the piping system between top of reactor and collection vial inlet. Utilizing continuous extraction was able to increase the extraction efficiency from less than 50% (batch process) to ~80%; therefore the later experiments were conducted with continuous extraction to achieve the highest efficiency.

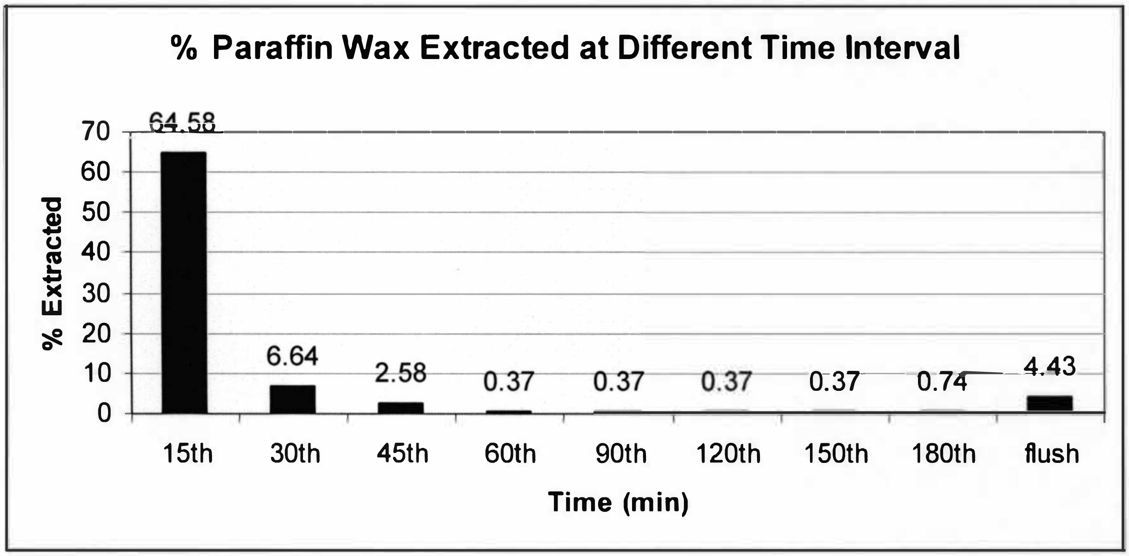

Figure 5: Percentages of paraffin wax extracted at different time interval for continuous extraction at 5000 psia, 100°C

Continuous extraction gave more promising results. A co-solvent, dichloromethane (CH_2Cl_2), was used to increase extraction efficiency. Table 7 shows the average percentage of paraffin wax extracted at 5000 psia and 100°C for three hours with and without using of co-solvent. The average extraction efficiency without using co-solvent is ~80%. After adding 5 ml of co-solvent to the extractor, the extraction efficiency becomes 90.25% or about ~10% increased.

Table 7: Continuous $ScCO_2$ extraction on paraffin wax

Trial #	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Pressure (psia)	5000	5000	5000	5000	5000	5000	5000	5000
Temp. (°C)	100	100	100	100	100	100	100	100
Co-solvent 5% volume	*none*	*none*	*none*	*none*	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
Sample Size (g.)	0.240	0.245	0.284	0.271	0.245	0.239	0.275	0.271
After extract 3 hr.								
Extracted Wt. (g.)	0.193	0.194	0.231	0.218	0.220	0.214	0.250	0.245
% Extracted	80.33	79.04	81.32	80.44	89.97	89.57	91.05	90.41
Average % Extracted	**80.28**				**90.25**			
Standard Deviation	0.94				0.63			

Tables 8 and 9 show data for continuous $ScCO_2$ extraction on hot-melt adhesive and PVAc respectively.

Table 8: Continuous $ScCO_2$ extraction on hot-melt adhesive

Trial #	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Pressure (psia)	5000	5000	5000	5000	5000	5000	5000	5000
Temp. (°C)	100	100	100	100	100	100	100	100
Co-solvent 5% volume	*none*	*none*	*none*	*none*	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
Sample Size (g)	0.272	0.270	0.284	0.277	0.267	0.269	0.047	0.438
After extract 3 hr.								
Extracted Wt. (g)	0.018	0.017	0.019	0.017	0.050	0.049	0.008	0.073
% Extracted	6.62	6.30	6.53	6.18	18.73	18.22	16.04	16.66
Average % Extracted	**6.41**				**17.41**			
Standard Deviation	0.20				1.27			

Table 9: Continuous $ScCO_2$ extraction on PVAc

Trial #	**1**	**2**	**3**	**4**	**5**	**6**
Pressure (psia)	5000	5000	5000	5000	5000	5000
Temp. (°C)	100	100	100	100	100	100
Co-solvent 5% volume	*none*	*none*	*none*	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
Sample Size (g)	1.353	1.360	1.397	1.335	1.387	1.356
After extract 3 hr						
Extracted Wt. (g)	0.063	0.068	0.066	0.115	0.124	0.115
% Extracted	4.66	4.981	4.72	8.61	8.95	8.48
Average % Extracted	**4.79**			**8.68**		
Standard Deviation	0.17			0.24		

Hot-melt adhesive and PVAc have low extraction efficiency. The extraction efficiencies were 6.41% for hot-melt adhesive and 4.79% for PVAc. After addition of 5 ml co-solvent, the $ScCO_2$ extraction efficiency improved to 17.41% and 8.41% respectively. Even though, there were significant improvements, the extraction efficiencies are still very low. Hot-melt adhesive contains a mixture of several compounds that were not dissolved in $ScCO_2$. Hot-melt adhesive samples were cut into tiny pieces before loaded inside the reactor. After the extraction, their color changed from yellow to lighter transparent yellow, but still keep their original shapes. This showed that the $ScCO_2$ fluid had penetrated into the pieces, due to its high diffusivity and extracted out the dissolvable compounds. Because of no dipole-dipole moment of CO_2, the sticky compounds that have high polarity showed low solubility in $ScCO_2$.

In the second part of the research, offset ink and gravure toluene base ink were used as the test subjects. First, the two ink samples were put in the 100°C oven until completely dry to determine the percentages of the ink can be evaporated in the actual printing process. Then, the new ink samples were put in the $ScCO_2$ reactor at 4000 psia, 40°C and extracted for two hours. The experimental results are shown in Table 15 and

16. The summary data are listed in Table 10.

Table 10: Printing ink percentages change by weight

Ink Type	Evaporated in oven (%)	$ScCO_2$ Extracted (%)
Gravure	49.69	49.46
Offset	6.46	28.03

Gravure ink contains mostly toluene solvent that quickly evaporates during printing. The percentage of gravure ink extracted was about equal to the percentage that evaporated in the oven. The solvent in the ink was quickly evaporated in both the heating oven and the $ScCO_2$ reactor. What remained were the solid dry inks. Offset ink is made up of a petroleum base that is very viscous. During printing, the ink reacts with oxygen in the air and polymerizes, hardening the ink film. In the $ScCO_2$ reactor, the $ScCO_2$ was able to extract 28.03% or 21.57% higher than oven dry. It was unknown which compounds were extracted. For both inks, after they came out from the reactor, the ink samples remained intact in the aluminum holder. As the result, $ScCO_2$ fluid extracted the solvent part, but did not have enough density to remove the ink particles, as was expected.

The third part of the research was to determine the $ScCO_2$ extraction efficiency on paraffin wax coated handsheets versus tensile strength of recycle handsheets. The first few handsheets were coated with paraffin wax and individually repulped (recycled) to make new handsheets, the tensile index values measured 31.32 N*m/g. This value represents the lowest possible tensile index value of the handsheet when the waxes were not removed. The experimental data are shown in Table 18 and the summary of tensile index results are listed in Table 11.

Table 11: Tensile index values for wax and non-wax coated handsheets

Group #	Wax Coated	Sc Extraction	Pressure (psia)	Temp. (°C)	% Wax Extracted	Tensile Index (N*m/g)
1	No	No	-	-	-	44.03
2	Yes	Yes	5000	50	85.18	41.21
3	Yes	Yes	5000	40	68.35	40.10
4	Yes	Yes	4000	50	85.77	42.62
5	No	Yes	5000	50	-	42.59
6	No	No	14.69	50	-	41.45

Group 1 has tensile index value of 44.03 N*m/g. Group 1 is the highest tensile index value that recycled handsheet can achieve when there is no contamination and no $ScCO_2$ treatment. In Group 2 and 3 were conducted at 5000 psia extraction pressure, the extraction efficiency increased from 68.35 to 85.18% as temperature increases from 40 to 50°C. In Group 4, the extraction condition was at 4000 psia and 50°C; it gave about the same extraction efficiency as in Group 2, but slightly higher tensile index value.

Group 5 was to determine the affect of $ScCO_2$ on the pure fibers. The tensile index values between Group 5 and 6 are almost identical. The handsheets that were put in the heating oven at atmospheric pressure and under supercritical condition did not show any change in the fiber tensile property. The handsheets in both groups stayed at 50°C condition for two hours.

The last part of the experiment was to focus on the effect of $ScCO_2$ to the fiber physical properties at three different temperatures (50, 80 and 105°C) at 5000 psia. All the handsheets from each group were exposed for two hours in the 2 L vessel. Each group was then repulped and remade into handsheets for physical property tests; tensile index, internal bond strength and zero-span breaking strength. The experimental tensile index data are shown in Table 19 and the summary of tensile index results are listed in Table 12 and Figure 6.

Table 12: Average tensile index values for pure recycled pulp handsheets from 2 L vessel

Group	Treatment	Tensile Index (N*m/g)
A	No Treatment	46.33
B	50°C 5000psia	49.12
C	80°C 5000psia	49.20
D	105°C 5000psia	47.53

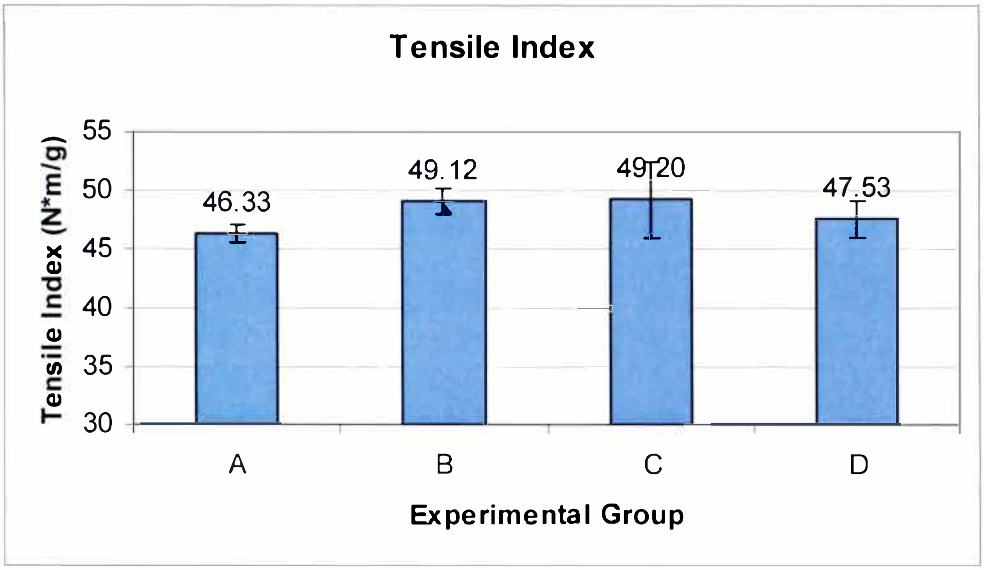

Figure 6: Average tensile index and standard deviation values for pure recycled pulp handsheets from 2 L vessel

Figure 6 shows a small increased in tensile index values with the $ScCO_2$ treated groups (B, C and D) when compare to group A that was not treated with $ScCO_2$ or exposed to any high temperature. This shows an opposite result as presented in Table 11, which showed a small decrease in tensile index value between groups 1 and 5. The differences in tensile index values in Table 11 and Figure 6 may be caused by the different experimental procedure. In the third part, a single handsheet was put into the 100 ml vessel for each experimental run and individually repulped and made into a new handsheet. On the other hand, the procedure for the last part was done by putting all 17 handsheets inside the 2 L vessels for one experimental run and together repulped all handsheets in that group and made into new handsheets. In Figure 6, the overall experimental values do not show any significant change to the fiber tensile strength with increasing vessel temperature.

The experimental internal bond strength (Scott type) data are shown in Table 20 and the summary of tensile index results are listed in Table 13 and Figure 7. Figure 7 shows similar trend as the tensile index data in Figure 6. This is because the two tests were testing the bonding strength of the paper. Tensile index is testing strength of paper in "x" and "y" directional planes. Internal bond strength test is testing the strength of paper in the "z" directional plane.

Table 13: Average internal bond strength values for pure recycled pulp handsheets from 2 L vessel

Group	Treatment	Internal Bond Strength (ft.*lbs.*10^{-3}/in.^{2})
A	No Treatment	80.01
B	50°C 5000psia	86.70
C	80°C 5000psia	84.10
D	105°C 5000psia	72.78

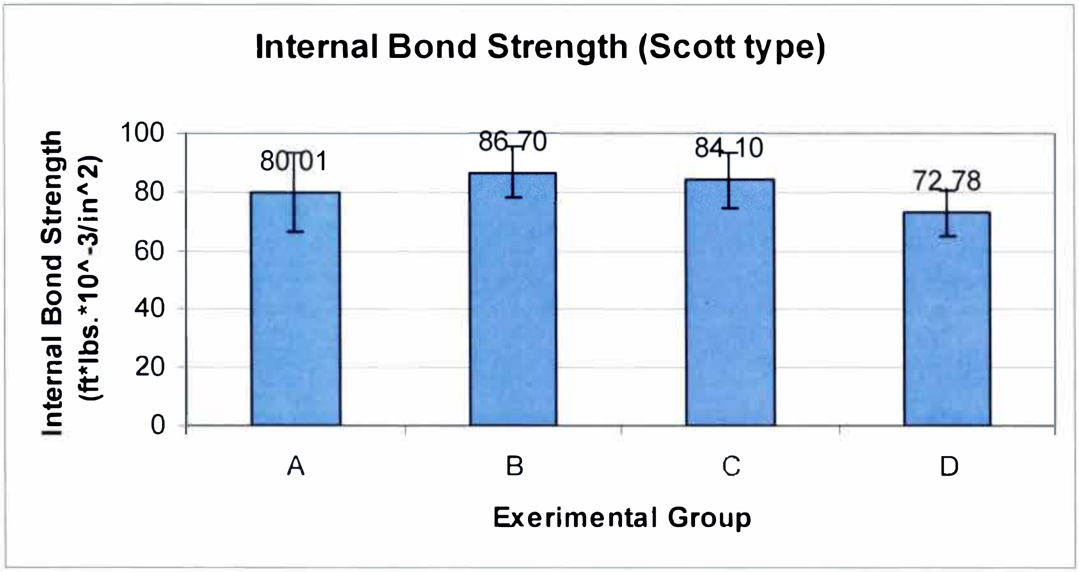

Figure 7: Average internal bond strength and standard deviation values for pure recycled pulp handsheets from 2 L vessel

The experimental zero-span breaking strength data are shown in Table 21 and the summaries of tensile index results are shown in Figures 8 to 11. In the zero-span measurement, it is impossible to measure direct zero-span value. Therefore, zero-span value can be extrapolated from several measured points with each point will have wider gap. In Figures 8 to 11, all figures show curves that behave as noise, which are very difficult to determine the trend line and estimate the true zero-span value.

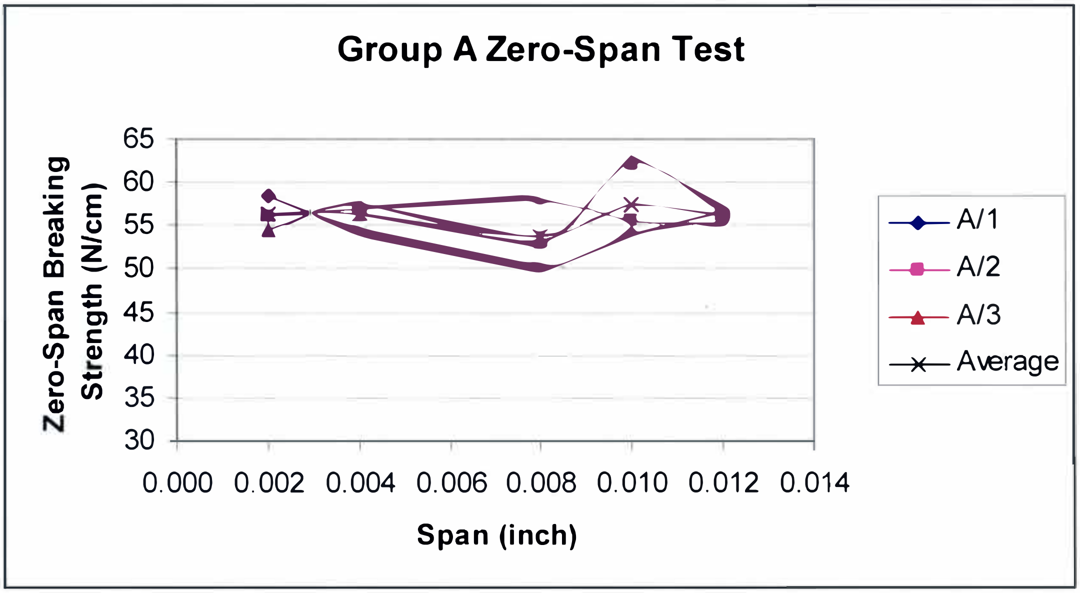

Figure 8: Zero-span breaking strength results for Group A handsheets

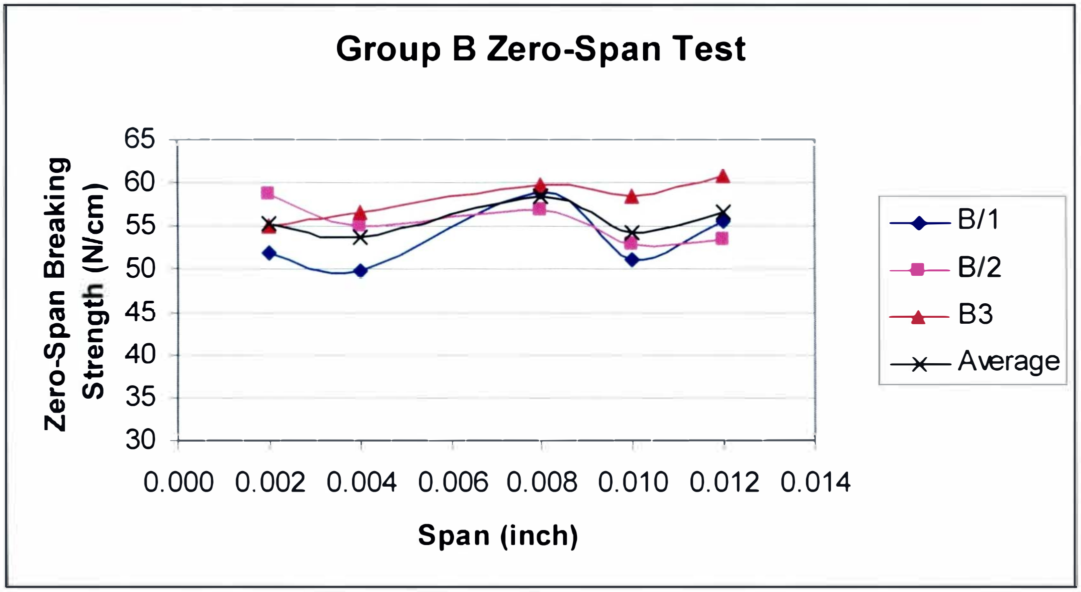

Figure 9: Zero-span breaking strength results for Group B handsheets

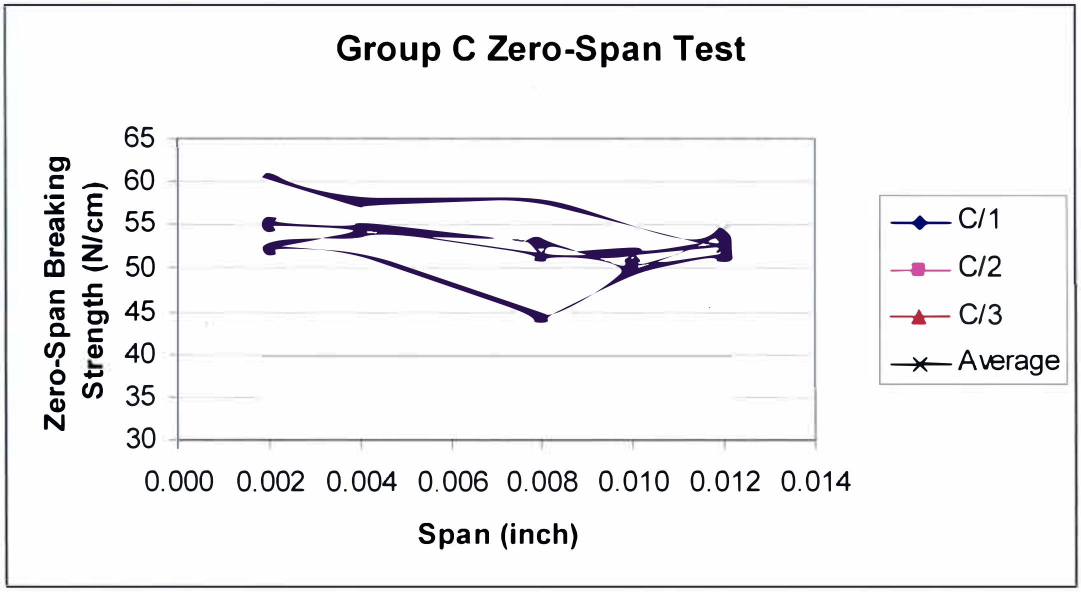

Figure 10: Zero-span breaking strength results for Group C handsheets

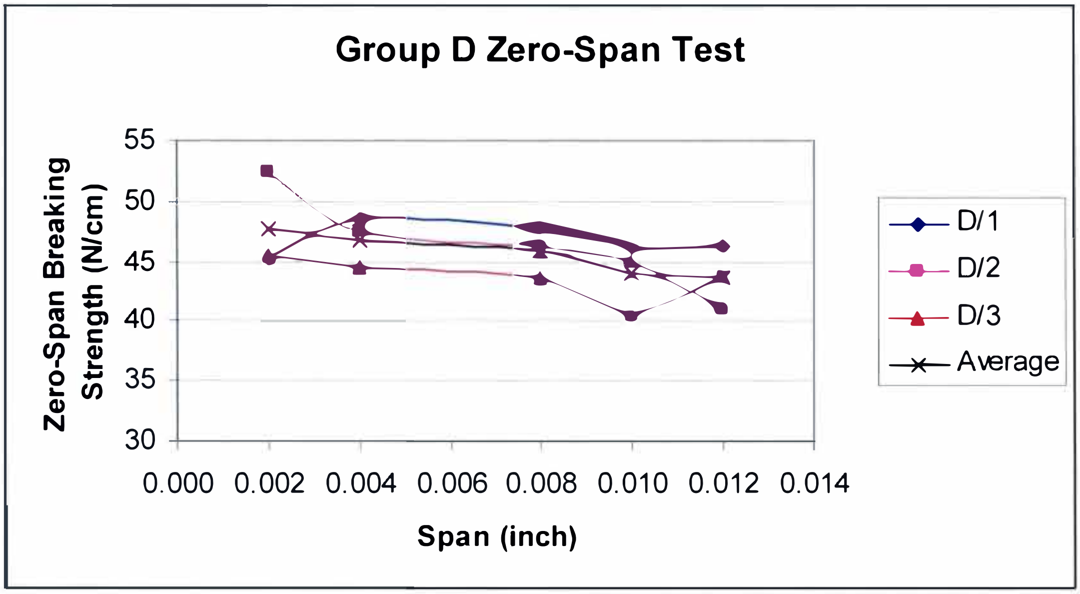

Figure 11: Zero-span breaking strength results for Group C handsheets

Figure 12 shows the average values for all zero-span reading from all tested handsheets. The figure shows that the reading values obtained from each group has very small standard deviation value. This means that the width of the span may not be far apart enough to distinguish significant different in readings and extrapolate the true zero-span value. Zero-span is measurement that measures fiber-breaking strength by eliminating the gap on the tested specimen. This will reduce the interaction of fiber-fiber bonding interaction and measure only the strength of fiber. Zero-span results are very important to identify if there is a direct physical change to the fiber or not.

The average value in Figure 12 for Group A, B and C show no significant different. As a result, putting handsheets under $ScCO_2$ at 50°C (Group B) and 80°C (Group C) have not effect to the physical strength property. In Group D, the average zero-span value is significantly lower than the rest of the groups. This result shows that under $ScCO_2$ condition at 105°C has reduced the fiber strength.

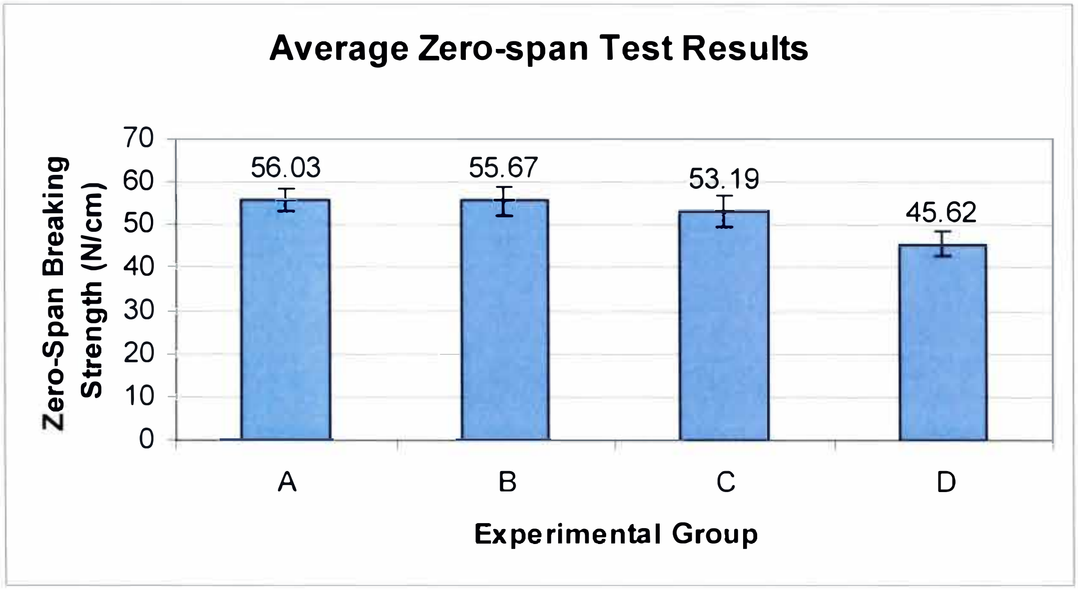

Figure 12: Average zero-span test results with standard deviation

As a result, from physical strength tests, $ScCO_2$ fluid has no affect on the fiber strength, but it is the temperature which accelerates the thermal degradations of fibers. In this experiment, a temperature of 105°C has the most affected on reducing the fiber strength as shown in Figure 12. Thermal degradation of paper is an irreversible process [15]. During the experiment, the handsheets were heated to high temperature, which evaporated the water molecules from the fibers. Driving off the water from the paper decreased the hydrogen bonding of water between fibers [1]. The heating effect also caused the thermal aging of paper. Thermal aging caused the paper to dry and became brittle.

CHAPTER VI

CONCLUSIONS

Initial investigation of supercritical fluid extraction equipment on sticky compounds demonstrated that the equipment was able of extracting sticky compounds; such as paraffin wax, hot-melt adhesive and PVAc. The equipment delivered high extraction efficiency on paraffin wax by utilizing a continuous process. In the batch process on the other hand, the reduction in pressure caused the solute compounds to deposit back inside the reactor, resulting in less extracting efficiency. Therefore, the continuous extracting process procedure was used throughout the study.

In the continuous process at 5000 psia and 50°C, the system delivered high efficiency with paraffin wax at ~80% without co-solvent and ~90% with addition of 5 ml dichloromethane as co-solvent. The extraction efficiencies on hot-melt adhesive and PVAc were 6.41% and 4.79% respectively without co-solvent. With addition of 5 ml co-solvent, the extraction efficiencies were triple on hot-melt adhesive and double on PVAc. The hot-melt adhesive contains several compounds that have very high molecular weight and are not soluble in $ScCO_2$. PVAc has very low solubility in $ScCO_2$. It will require longer extraction time and an agitating mechanism in the reactor to achieve higher efficiency.

In second part of the study, $ScCO_2$ extraction was not able to extract and remove ink particles from inside the reactor. The ink samples were dry and tightly held together in the sample holders. It is still unknown whether the $ScCO_2$ fluid is unable to extract ink particles or the equipment requires an agitating mechanism to disperse the particles in the reactor in order to increase the extraction efficiency.

In the third part of the study, it was clearly shown that the extraction efficiency is more dependent on temperature than pressure. When the coated handsheets were extracted at 50°C, they gave the about the same extraction efficiencies when extracted at 4000 or 5000 psia pressures. The extraction efficiency dropped significantly when the extraction temperature changed to 40°C and the extraction pressure was maintained at 5000 psia.

In the last part of the research, the handsheets were treated with $ScCO_2$ at three different temperatures for two hours and compared the results with the untreated with $ScCO_2$. The handsheets were recycled and made into handsheets for three physical strength tests; tensile index, internal bond strength and zero-span breaking strength. The results show that $ScCO_2$ fluid has no effect to fiber physical strength at temperature ≤80°C and extreme pressure of 5000 psia. At 105°C, the fibers showed a reduction in fiber strength on the zero-span breaking strength test. The tensile index and internal bond strength tests showed no significant reduction in fiber bonding strengths of the handsheets at all temperatures.

Carbon dioxide is environmentally friendly, recyclable, and has 100% separation between extracted compounds and CO_2 gas. Utilizing $ScCO_2$ fluid extraction to removing sticky compounds from the recycled paper before the deinking process will increase the purity of the recycled pulp. This will benefit in reducing the sticky problems in the paper mills and possibly decreasing of addition of virgin pulp to recycled paper products.

CHAPTER VII

RECOMMENDATION

For future experiment, it is recommended to test the effect of $ScCO_2$ fluid to the fiber physical strength with time. In this experiment, maximum two hours for the tested samples to stay inside the reactor vessel may not be long enough to monitor the full affect of $ScCO_2$ fluid to the fiber properties.

It is also recommended to conduct the zero-span breaking strength test with larger span gap on a specimen. This would increase the accuracy of the curve and be able to extrapolate the true zero-span value. More handsheets are also required to conduct the experiment and tests without shortage in specimens.

Table 14: $ScCO_2$ batch process extraction efficiency and condition on paraffin wax.

Trial #	1	2	3	4	5	6	7	8
Pressure (psia)	4000	4000	4000	4000	4000	6000	6000	6000
Temp. (°C)	40	40	40	40	40	40	40	40
Sample Size (g)	0.272	0.282	0.278	0.271	0.576	0.280	0.278	0.284
Vial initial wt. (g)	25.14	25.143	25.078	25.145	25.143	25.085	122.959	24.697
After extract 1 hr.								
Vial final wt. (g)	25.202	25.187	25.133	25.199	25.224	25.192	123.066	24.796
Extracted Wt. (g)	0.062	0.044	0.055	0.054	0.081	0.107	0.107	0.099
% Extracted	22.79	15.60	19.78	19.93	14.06	38.21	38.49	34.86
Average % Extracted	18.43					37.19		

Trial #	9	10	11	12	13	14
Pressure (psia)	7000	7000	7000	4000	4000	4000
Temp. (°C)	40	40	40	55	55	55
Sample Size (g)	0.291	0.268	0.267	0.281	0.286	0.282
Vial initial wt. (g)	24.697	25.003	24.974	25.139	24.719	24.979
After extract 1 hr.						
Vial final wt. (g)	24.796	25.097	25.064	25.209	24.802	25.062
Extracted Wt. (g)	0.099	0.094	0.09	0.07	0.083	0.083
% Extracted	34.02	35.07	33.71	24.91	29.02	29.43
Average % Extracted	34.27			27.79		

Trial #	15	16	17	18	19	20	21
Pressure (psia)	4000	4000	4000	4000	5000	5000	5000
Temp. (°C)	65	65	65	65	75	75	75
Sample Size (g)	0.270	0.286	0.281	0.278	0.281	0.285	0.286
Vial initial wt. (g)	25.042	25.12	25.094	25.019	24.947	25.110	25.106
After extract 1 hr.							
Vial final wt. (g)	25.131	25.215	25.170	25.119	25.055	25.216	25.205
Extracted Wt. (g)	0.089	0.095	0.076	0.1	0.108	0.106	0.099
% Extracted	32.96	33.22	27.05	35.97	38.43	37.19	34.62
Average % Extracted	32.30				36.75		

Trial #	22	23	24
Pressure (psia)	5000	5000	5000
Temp. (°C)	90	90	90
Sample Size (g)	0.283	0.285	0.275
Vial initial wt. (g)	25.081	25.098	25.057
After extract 1 hr.			
Vial final wt. (g)	25.211	25.247	25.185
Extracted Wt. (g)	0.13	0.149	0.128
% Extracted	45.94	52.28	46.55
Average % Extracted	48.25		

Table 15: Mass percentages of ink evaporated in 100°C oven.

Ink Type	**Offset Ink**			**Gravure Ink**		
Cup holder wt. (g)	2.115	2.134	2.143	0.047	0.041	0.052
Cup + Ink wt. (g)	2.989	2.914	3.233	0.286	0.371	0.452
Ink wt. (g)	0.874	0.78	1.09	0.239	0.330	0.401
After oven dry						
Cut + Ink wt. (g)	2.933	2.862	3.165	0.167	0.205	0.255
Dry Ink wt. (g)	0.818	0.728	1.022	0.120	0.165	0.203
% Solid	93.52	93.33	93.76	50.44	49.91	50.59
% Solvent evaporated	6.48	6.67	6.24	49.56	50.09	49.41
Average % Extracted	6.46			50.31		
Standard Deviation	0.22			0.36		

Table 16: $ScCO_2$ extraction efficiency and condition on commercial printing inks.

Ink Type	**Offset Ink**					**Gravure Ink**		
Pressure (psia)	4000	4000	4000	4000	4000	40	40	40
Temp (°C)	40	40	40	40	40	4000	4000	4000
Extracted time (hr)	2	2	2	2	2	2	2	2
Holder wt (g)	0.051	0.050	0.049	0.049	0.050	0.047	0.031	0.045
Holder + ink wt. (g)	0.179	0.165	0.188	0.184	0.177	0.341	0.282	0.33
Sample ink wt. (g)	0.128	0.115	0.139	0.135	0.127	0.294	0.251	0.285
After extracted								
Holder + ink wt. (g)	0.129	0.133	0.156	0.147	0.148	0.195	0.152	0.187
Ink final wt (g)	0.078	0.083	0.107	0.098	0.098	0.148	0.121	0.142
Change in wt. (g)	0.050	0.032	0.032	0.037	0.029	0.146	0.130	0.143
% Extracted	39.06	27.83	23.02	27.41	22.83	49.66	51.79	50.18
Average % Extracted	28.03					50.54		
Standard Deviation	6.60					1.11		

Table 17: $ScCO_2$ extraction efficiency and condition on paraffin wax coated handsheets.

Group #	Handsheet wt. (g)	Wax wt. (g)	Moisture Content (g)	Total wt. (g)	$ScCO_2$ Extraction	Pressure (psia)	Temp. (°C)	After Extraction Sample wt. (g)	Δ wt. (g)	Extracted (%)
1	1.150	0	0.092	1.150	No	-	-	-	-	-
1	1.270	0	0.102	1.270	No	-	-	-	-	-
1	1.240	0	0.099	1.240	No	-	-	-	-	-
1	1.290	0	0.103	1.290	No	-	-	-	-	-
1	1.240	0	0.099	1.240	No	-	-	-	-	-
2	1.294	0.322	0.104	1.616	Yes	5000	50	1.240	0.272	84.58
2	1.311	0.448	0.105	1.759	Yes	5000	50	1.272	0.382	85.27
2	1.276	0.456	0.102	1.732	Yes	5000	50	1.239	0.391	85.70
2	1.299	0.341	0.104	1.640	Yes	5000	50	1.256	0.280	82.10
2	1.255	0.444	0.101	1.699	Yes	5000	50	1.216	0.382	86.14
3	1.327	0.473	0.106	1.800	Yes	5000	40	1.333	0.361	76.26
3	1.242	0.340	0.099	1.582	Yes	5000	40	1.241	0.242	71.03
3	1.266	0.455	0.101	1.721	Yes	5000	40	1.261	0.359	78.81
3	1.289	0.446	0.103	1.735	Yes	5000	40	1.365	0.267	59.81
3	1.315	0.413	0.105	1.728	Yes	5000	40	1.392	0.231	55.85
3	1.265	0.477	0.101	1.742	Yes	5000	40	1.285	0.356	74.56
3	1.305	0.436	0.105	1.741	Yes	5000	40	1.322	0.314	72.13
4	1.282	0.423	0.103	1.705	Yes	4000	50	1.243	0.359	84.94
4	1.312	0.470	0.105	1.782	Yes	4000	50	1.270	0.407	86.58
4	1.298	0.412	0.104	1.710	Yes	4000	50	1.258	0.348	84.47
4	1.304	0.484	0.104	1.788	Yes	4000	50	1.262	0.422	87.10
5	1.309	0	0.105	1.309	Yes	5000	50	1.263	0.046	3.51
5	1.279	0	0.102	1.279	Yes	5000	50	1.243	0.036	2.81
5	1.259	0	0.101	1.213	Yes	5000	50	1.213	0.046	3.65
5	1.308	0	0.105	1.265	Yes	5000	50	1.265	0.043	3.29
5	1.267	0	0.101	1.267	Yes	5000	50	1.230	0.037	2.92
6	1.220	0	0.098	1.220	No	14.69	50	1.164	0.056	4.59
6	1.262	0	0.100	1.250	No	14.69	50	1.194	0.068	5.39
6	1.300	0	0.104	1.300	No	14.69	50	1.234	0.066	5.08
6	1.275	0	0.102	1.270	No	14.69	50	1.216	0.059	4.63
6	1.141	0	0.091	1.140	No	14.69	50	1.088	0.053	4.65
6	1.284	0	0.103	1.290	No	14.69	50	1.231	0.053	4.13

Table 18: Recycled handsheet tensile index values utilized 100 ml vessel.

Group #	Handsheet wt. (g)	Handsheet Basis wt. (g/m^2)	Tensile value (N/m)								Tensile index (N*m/g)
			1	2	3	4	5	6	7	Average	
1	1.150	57.50	2.795	3.205	3.839	3.584	3.801	3.987		3.535	40.20
1	1.270	63.50	5.136	4.746	4.628	4.438	4.354			4.660	47.98
1	1.240	62.00	4.268	4.588	4.086	3.987	4.599			4.306	45.40
1	1.290	64.50	4.456	4.344	4.293	4.271	4.510	4.795		4.445	45.05
1	1.240	62.00	3.992	3.627	3.978	3.519	4.303	4.196		3.936	41.50
2	1.294	62.00	3.761	4.131	3.976	3.780	3.965	3.315		3.821	40.30
2	1.311	63.50	3.603	4.427	3.702	3.788	4.172	4.421		4.019	41.38
2	1.276	62.50	4.177	4.311	3.348	3.941	4.18	4.099		4.009	41.94
2	1.299	64.00	3.783	3.860	4.212	3.876	3.442			3.835	39.17
2	1.255	62.00	2.811	3.060	3.989	4.660	4.435	4.250		3.868	40.78
3	1.327	69.50	2.897	3.085	3.721	4.225	4.26	3.366	4.287	3.692	34.73
3	1.242	64.50	4.207	4.231	4.797	4.293	4.703	4.376		4.435	44.95
3	1.266	62.50	4.752	3.71	4.572	4.223	4.346	4.451		4.342	45.42
3	1.289	61.00	3.683	3.356	3.044	3.06	2.588	3.321		3.175	34.03
3	1.315	68.00	4.344	4.368	4.008	4.016	4.523	4.553		4.302	41.36
3	1.265	63.25	4.070	3.310	4.556	3.817	3.919	3.648		3.887	40.18
3	1.305	65.25	3.839	4.491	4.609	4.293	4.727	4.443		4.400	44.09
4	1.282	63.00	4.531	4.268	3.968	3.968	3.587			4.064	42.18
4	1.312	64.50	3.74	3.893	3.804	4.314	4.531	3.643		3.988	40.42
4	1.298	64.00	3.809	4.18	4.709	4.354	4.059	4.499		4.268	43.60
4	1.304	65.00	4.054	4.242	4.856	4.327	4.483	4.456		4.403	44.29
5	1.309	60.50	4.011	3.393	3.57	3.863	3.6	3.509	3.417	3.623	39.16
5	1.279	62.00	3.764	4.255	4.121	3.844	3.831	4.582	3.544	3.992	42.09
5	1.259	61.15	3.686	4.789	4.915	4.166	4.54	3.519		4.269	45.64
5	1.308	65.00	3.807	4.564	4.387	4.376	4.548	4.255		4.323	43.48
5	1.267	62.00	4.038	3.235	4.36	3.748	4.295	3.968		3.941	41.55
6	1.220	61.00	3.35	4.322	3.952	3.917	3.831	3.992		3.894	41.74
6	1.262	62.50	3.834	3.774	3.906	4.459	4.113	4.685		4.129	43.19
6	1.300	65.00	4.075	4.107	3.342	3.836	4.242	4.352		3.992	40.16
6	1.275	63.50	4.701	3.801	4.258	4.572	3.493			4.165	42.88
6	1.141	57.00	3.517	2.848	4.263	3.611	3.358	3.801		3.566	40.91
6	1.284	64.50	3.546	4.11	4.003	3.651	3.858	4.408		3.929	39.83

Table 19: Recycled handsheet tensile index values utilized 2 L vessel.

Group #	Handsheet wt. (g)	Handsheet Basis wt. (g/m^2)	Tensile values (N/m)						Tensile Index (N*m/g)		
			1	2	3	4	5	Average	Tensile index	Average	Std. Dev.
A	1.247	62.35	5.95	4.14	3.69	4.38	4.31	4.49	47.11	46.33	0.71
A	1.252	62.60	4.81	4.71	3.99	4.14	4.24	4.38	45.72		
A	1.342	67.10	4.44	4.80	4.71	4.72	5.02	4.74	46.15		
B	1.377	68.85	5.41	4.78	5.50	5.54	5.22	5.29	50.25	49.12	1.10
B	1.339	66.95	5.43	4.96	4.23	4.78	5.72	5.02	49.07		
B	1.259	62.95	4.44	5.14	4.94	4.11	4.51	4.63	48.05		
C	1.361	68.05	5.24	5.51	4.87	5.77	5.28	5.33	51.24	49.20	3.21
C	1.326	66.30	5.34	5.05	5.09	5.37	4.95	5.16	50.86		
C	1.261	63.05	4.60	4.64	4.34	4.05	4.31	4.39	45.51		
D	1.320	66.00	4.69	5.24	5.03	4.97	4.95	4.97	49.28	47.53	1.52
D	1.352	67.60	4.72	4.87	4.78	5.07	4.69	4.82	46.65		
D	1.343	67.15	4.64	4.48	4.57	5.00	5.27	4.79	46.65		

Table 20: Recycled handsheet internal bond strength values utilized 2 L vessel.

	Group A HS#				Group B HS#			
	Internal Bond Strength (ft.*lbs.*10^{-3}/in.^{2})				Internal Bond Strength (ft.*lbs.*10^{-3}/in.^{2})			
Test Strip	1	2	3	4	1	2	3	4
1	99.5	85	80	85	86	80	79	81
2	95	101	86	65	78	85	90	83
3	77	86	95	60	86	91	97	108
4	84	77	90	55	80	81	85	82
5	90	82	85	54	90	85	85	80
6	79	70	76	83	85	85	83	80
7	78	93	83	89	85	83	92	99
8	54	76	102	89	90	88	113	90
9	54	76	83	76	89	73	95	88
10	54	79	80	95	94	84	65	95
HS Average	76.45	82.50	85.56	75.10	86.30	83.50	88.40	88.60
Total Average	80.01				86.70			
Total Std. Dev.	13.25				8.51			

	Group C HS#				Group D HS#			
	Internal Bond Strength (ft.*lbs.*10^{-3}/in.^{2})				Internal Bond Strength (ft.*lbs.*10^{-3}/in.^{2})			
Test Strip	1	2	3	4	1	2	3	4
1	86	75	85	95	68	66	70	68
2	100	89	97	105	91	85	84	85
3	89	74	76	100	56	72	71	76
4	80	80	81	105	75	74	71	79
5	76	79	75	95	70	75	55	79
6	80	81	76	80	65	66	64	66
7	90	101	86	92	81	89	80	75
8	76	78	79	79	75	70	67	70
9	77	76	78	82	74	68	70	71
10	81	75	80	75	75	70	70	75
HS Average	83.50	80.80	81.30	90.80	73.00	73.50	70.20	74.40
Total Average	84.10				72.78			
Total Std. Dev.	9.20				7.68			

Table 21: Recycled handsheet zero-span breaking strength values utilized 2 L vessel.

Group/HS #	Test Strip	Gap (inch)	Wt. (g)	Basis wt. (g/m^2)	Measured value (psi)	Zero-span N/cm	Corrected N/cm
A/1	1	0.002	0.102	64.76	26.0	63.06	58.43
	2	0.004	0.102	64.76	24.3	58.94	54.61
	3	0.008	0.103	65.40	22.6	54.82	50.29
	4	0.010	0.100	63.49	23.6	57.24	54.09
	5	0.012	0.099	62.86	24.5	59.43	56.72
A/2	1	0.002	0.105	66.67	25.7	62.34	56.10
	2	0.004	0.103	65.40	25.6	62.09	56.97
	3	0.008	0.105	66.67	26.6	64.52	58.07
	4	0.010	0.103	65.40	25.0	60.64	55.63
	5	0.012	0.102	64.76	24.6	59.67	55.28
A/3	1	0.002	0.105	66.67	25.0	60.64	54.57
	2	0.004	0.102	64.76	25.6	62.09	57.53
	3	0.008	0.099	62.86	23.0	55.79	53.25
	4	0.010	0.103	65.40	28.0	67.91	62.31
	5	0.012	0.102	64.76	25.2	61.12	56.63
B/1	1	0.002	0.105	66.67	23.8	57.73	51.95
	2	0.004	0.106	67.30	23.0	55.79	49.73
	3	0.008	0.105	66.67	27.0	65.49	58.94
	4	0.010	0.103	65.40	23.0	55.79	51.18
	5	0.012	0.104	66.03	25.2	61.12	55.54
B/2	1	0.002	0.107	67.94	27.4	66.46	58.70
	2	0.004	0.105	66.67	25.2	61.12	55.01
	3	0.008	0.104	66.03	25.8	62.58	56.86
	4	0.010	0.104	66.03	24.0	58.21	52.89
	5	0.012	0.103	65.40	24.0	58.21	53.41
B/3	1	0.002	0.105	66.67	25.2	61.12	55.01
	2	0.004	0.105	66.67	26.0	63.06	56.76
	3	0.008	0.108	68.57	28.2	68.40	59.85
	4	0.010	0.105	66.67	26.8	65.00	58.50
	5	0.012	0.108	68.57	28.6	69.37	60.70

Table 21 - Continued

Group/HS #	Test Strip	Gap (inch)	Wt. (g)	Basis wt. (g/m^2)	Measured value (psi)	Zero-span N/cm	Corrected N/cm
C/1	1	0.002	0.106	67.30	28.0	67.91	60.55
	2	0.004	0.103	65.40	26.0	63.06	57.86
	3	0.008	0.103	65.40	26.0	63.06	57.86
	4	0.010	0.105	66.67	25.0	60.64	54.57
	5	0.012	0.102	64.76	23.5	57.00	52.81
C/2	1	0.002	0.102	64.76	23.3	56.51	52.36
	2	0.004	0.102	64.76	24.0	58.21	53.93
	3	0.008	0.102	64.76	23.6	57.24	53.03
	4	0.010	0.100	63.49	22.0	53.36	50.43
	5	0.012	0.101	64.13	23.8	57.73	54.01
C/3	1	0.002	0.104	66.03	23.8	57.73	52.45
	2	0.004	0.105	66.67	23.8	57.73	51.95
	3	0.008	0.105	66.67	20.4	49.48	44.53
	4	0.010	0.102	64.76	22.2	53.85	49.89
	5	0.012	0.102	64.76	23.0	55.79	51.68
D/1	1	0.002	0.098	62.22	19.4	47.05	45.37
	2	0.004	0.099	62.86	20.9	50.69	48.39
	3	0.008	0.098	62.22	20.4	49.48	47.71
	4	0.010	0.098	62.22	19.8	48.03	46.31
	5	0.012	0.099	62.86	20.0	48.51	46.31
D/2	1	0.002	0.105	66.67	24.0	58.21	52.39
	2	0.004	0.105	66.67	21.8	52.88	47.59
	3	0.008	0.105	66.67	21.2	51.42	46.28
	4	0.010	0.103	65.40	20.2	49.00	44.95
	5	0.012	0.104	66.03	18.6	45.11	40.99
D/3	1	0.002	0.106	67.30	21.0	50.94	45.41
	2	0.004	0.104	66.03	20.2	49.00	44.52
	3	0.008	0.104	66.03	19.8	48.03	43.64
	4	0.010	0.107	67.94	19.0	46.08	40.70
	5	0.012	0.108	68.57	20.6	49.97	43.72

REFERENCES

1. Phelps, C. L., Smart, N. G., & Wai, C. M. (1996). Past, present, and possible future applications of supercritical fluid extraction technology. Journal of Chemistry Education, 73, 1163-1168.

2. Blaney, C. A. & Hossain, S. U. (1991). U.S. Patent 5 074 958

3. Blaney, C. A. & Hossain, S. U. (1991). U.S. Patent 5 009 746

4. Eckert, C. A., Knutson, B. L., & Debenedetti, P. G. (1996). Supercritical fluids as solvents for chemical and material process. Nature, 383, 313.

5. McHugn, M. A., & Krukonis, V. J. (1994). Supercritical fluids extraction: principles and practice, 2nd, Stoneham, MA

6. Doshi, M. R. (1987). Cleaning and screening. In Kocurek M. J. (Eds.), Pulp and Paper Manufacture, 3rd, (pp. 189-205). Atlanta, GA: TAPPI

7. Orthner, H. E. (1987). Flotation Deinking. In Kocurek M. J. (Eds.), Pulp and Paper Manufacture, 3rd, (pp. 206-220). Atlanta, GA: TAPPI

8. Wikipedia: Supercritical fluid. (2006, April 26). Retrieved April 1, 2006, from http://en.wikipedia.org/wiki/Supercritical_fluid

9. Leeds Cleaners Synthesis Group: Solvent properties of supercritical fluids. (2001, January 23. Retrieved April 1, 2006, from http://www.chem.leeds.ac.uk/People/CMR/index.html

10. Ramsey, E. D. (1998). Analytical supercritical fluid extraction techniques. Norwell, MA: Kluwer Academic Publishers

11. Zhang, X., Han, B., & Hou, Z. (2002). “Why do co-solvents enhance the solubility of solutes in supercritical fluids?”, Chemical Engineering Journal, 8, 22.

12. Peel, J. D., (1999). Paper science and paper manufacture. Bellingham, WA: Angus Wilde Publication Inc.

13. Rong, X., Qi, D., Chateuneuf, J., & Abubakr, S. (2005). Study of co-solvent effects on stickies removal in supercritical fluid extraction. 2005 TAPPI Coating Conference

14. Organic Chemistry: Solvents. (n.d.). Retrieved April 1, 2006, from http://www.usm.maine.edu/~newton/Chy251_253/Lectures/Solvents/Solvents.html

15. Stamm A. J. (1956). Thermal degradation of wood and cellulose. Industrial and Engineering Chemistry, 48(3), 413-417.