SELECTIVE DEPOLYMERIZATION OF INDUSTRIAL HEMP AND ITS EFFECTS ON THERMAL RESISTIVITY

A Senior Project

presented to

the Faculty of the Materials Engineering Department

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of the Requirements for the Degree

Bachelor of Science, Materials Engineering

by

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Abstract

There is a growing shift within the construction materials industry towards green and sustainable building products. Spending in this area has increased 5-fold since 2011 to a total revenue of $70 billion. An area of interest has been aimed at replacing fiberglass batt insulation with cellulose. Cellulose is the most abundant polymer on earth, and has potential to replace petroleum derived insulations. This project explores the potential of selectively isolating cellulose by depolymerizing the support structures found in lignocellulosic materials – specifically lignin and hemicellulose. The current focus is on isolating cellulose from *Cannabis sativa*, but more specifically, industrial hemp. Previous studies have successfully delignified industrial hemp using chlorite as a nucleophile that can selectively dissolve lignin and hemicellulose, but not cellulose. However, no study to date has explored the effects of selective depolymerization and its effects on thermal insulation (R-value). By selectively dissolving support biopolymers away from cellulose, it should induce macro and nano-scale pores within the cellulose matrix – a change that may increase thermal resistivity. The project has characterized depolymerized industrial hemp with materials characterization techniques such as: Scanning Electron Microscopy, Thermal Gravimetric Analysis, X-ray Diffraction, and Fourier Transform Infrared Spectroscopy. Third party laboratory testing was conducted at RADCO Laboratories to determine insulating performance by adhering to ASTM C518. Untreated industrial hemp had an R value of $2.4 \text{ } Hr \times ft^2 \times ^\circ F/\text{BTU}$ and the depolymerized hemp had an R value of $2.7 \text{ } Hr \times ft^2 \times ^\circ F/\text{BTU}$.
1.0 Introduction

1.1 DTE Materials

I have been working on this project of finding a cellulose derived insulating material since December 2015. The prototype has taken on a multitude of iterations with every new discovery. The current, and likely final, iteration of this minimum viable product is cellulose dense pack blow-in insulation derived from industrial hemp. What began as purely research has now pivoted to an entrepreneurial endeavor. I formed a company called DTE Materials (Down to Earth), and have been developing my business skills through Cal Poly’s CIE program including the on-campus incubator (The Hatchery), the summer accelerator program at the Hot House, and entrepreneurship classes and coaching from VentureWell E Team Programs. The focus of this senior project was to test a hypothesis of chemically altering cellulose for the purposes of increasing thermal insulating performance. The findings and data divulged have been claimed by DTE Materials, and are patent pending as of May 25, 2017.

1.2 Value Proposition

A fundamental need within the residential and commercial construction industries for alternatives to petroleum and fiberglass based insulation has been identified. The 3 key pain points associated with fiberglass are: toxicity and health concerns, degrading performance over time, and installation times in attics and at large scale.

Major shortcomings identified with current insulation are:
- Health concerns – OSHA labeled hazard, sick building syndrome
- Efficiency degradation over time due to susceptibility to vapor
- Thermal bridges and reducing efficiency
- Installation time and hazards of handling
- Carbon Emissions

OSHA has deemed petroleum and fiberglass forms of insulation as potential carcinogens because of the small glass fibers that are easily inhaled. Direct from the OSHA website: “Inhalation of fiberglass material has been linked to cancer by OSHA, IARC (International Agency for Research on Cancer), and NTP (National Toxicology Program).” DTE (Down to Earth) Materials looks to disrupt the insulation market with a product that will be addressing many health issues, performance, and installation faults.

Potential answers to this fundamental need for healthy and high performance forms of insulation are currently being explored. Proposed solutions include the shift towards greener fiberglass- although consistently petroleum based, or 3 entirely new materials more suited for sustainability all together. The latter option involves the scope of this project to truly address the problem statement by developing a long-term solution that will not need to be revisited. The alternative DTE Materials looks to explore involves cellulose-based insulation. Cellulose-based insulation was a leading candidate due to its inherent thermal insulating properties, its natural antibacterial and vapor resilience, and to help alleviate the carbon intensive processes associated with fiberglass synthesis.

I chose to pursue industrial hemp hurd as the source of cellulose for many reasons. Hemp is a fast-growing plant that can be cultivated multiple times per year (3) and is also easy to cultivate¹. This is in direct contrast to current forms of cellulose insulations that often have recycled paper which are unfortunately sourced from tree deforestation. This is much less sustainable since trees require more time and energy resources to cultivate. The switch to industrial hemp for use of cellulose insulation would promote the creation of oxygen into the atmosphere through its growth, something that isn’t provided
through current cellulose insulations. Industry standard for cellulose blow-in insulation utilizes recycled newspaper that needs to have the ink and metals removed from it prior to use. A study conducted by the United States Department of Agriculture proved that hemp can produce 410% more cellulose per acre relative to trees. Hemp hurd is the inner, woody part of the hemp plant, and is one of the more underutilized parts of the hemp plant that tends to be considered a waste product or used for animal bedding. By using hemp hurd for cellulose insulation, we will be creating a new use for the material while also creating other valuable coproducts, such as plastics and sugars due to my patent pending chemical treatment.

### 1.3 Project Goals

This project is focused on the development of an insulating material from industrial hemp. The first point of development was in finding a repeatable process from literature for selectively depolymerizing the cellulosic chemistry of the hemp that would induce anatomical changes. Materials characterization techniques were then used to analyze the changes induced by the removal of lignin and hemicellulose: Scanning Electron Microscopy (visual changes), X-ray Diffraction (% crystallinity), Fourier Transform Infrared Spectroscopy (functional groups and H bonding), and Thermal Gravimetric Analysis (% composition). The control sample and the depolymerized sample were tested for insulating performance per ASTM C518.

### 2.0 Background

#### 2.1 Cellulosic Material

Cellulosic material refers to the broader category of materials that is comprised of three biopolymers: majority cellulose, hemicellulose, and lignin. Cellulose is a polysaccharide of β 1,4 glucose linkages, and hemicellulose is also a polysaccharide of β 1,4 xylose linkages. These linkages are presented in Figure 1 (section a) as the carbon-oxygen-carbon noncyclic single bonds. Lignin is comprised of linked polyphenols/alcohols with different ortho-substituents, and are shown in section b of Figure 1. The type of lignin and compositional makeup of the biopolymers depends on the type of wood. The most common

![Figure 1. Lignin and hemicellulose provide secondary structural support by binding to cellulose through hydrogen bonding mechanisms.](image-url)
types of woods are softwood, hardwood, and grasswoods. Industrial hemp is categorized as a perennial grasswood. Hemp hurd is comprised of 40-48% cellulose, 18-24% hemicellulose, and 21-24% lignin. This is significantly different than the hemp fiber which typically has lower lignin concentrations: 57-77% cellulose, 9-14% hemicellulose, and 5-9% lignin. In choosing to pursue the hemp hurd specifically, the higher lignin concentration should theoretically result in a higher increase in porosity – the mechanisms of which will be discussed within. The purpose of cellulose is to provide the bulk of the structural support especially along the longitudinal direction. Lignin and hemicellulose provide secondary structural support, and protection between the cellulose fibrils by hydrogen bonding mechanisms.

2.2 Selective Depolymerization

The hypothesis, and ultimately the goal of this project, is to qualify the following statement: thermal resistivity of cellulose-based insulation from hemp shiv can be increased by introducing micro and nanoscale air pockets within the lignocellulose matrix. Two underlying philosophies must be confirmed in order for the hypothesis to be qualified. The first is the introduction of nanopores, where the lignin and hemicellulose used to reside within the matrix. This assumption is based on the idea that when a component of a given volume is removed from a system, ambient air will fill in the space where the component was previously situated within the system. Secondly, the removal of two supporting structures from the cellulose system should in theory induce separation of cellulose fibrils. This should produce macroscopic voids between cell walls, specifically in the middle lamella region which has high lignin content and previously existing air spaces. The removal of the high lignin content from this region should induce cellulose agglomeration which would cause receding between cell walls which should increase porosity. In this instance, it is imperative to maintain the cellulose fibril orientation and structure. If this cellulose structure breaks down, then the opportunity to add macro scale air pockets is in turn lost. The percent of lignin and hemicellulose removal while maintaining the cellulose matrix will be the treatment variable within this project. The goal will be to maximize or achieve a working percentage of cellulose, hemicellulose, and lignin. Figure 2 demonstrates the increased porosity within the cellulose matrix after removal of lignin using Kraft bleaching techniques. These images were obtained from a delignification study of transparent wood at the KTH Royal Institute of Technology.

Figure 2. The top two SEM images (b,c) are prior to depolymerization. The results of depolymerization are shown below (d,e), as porosity has increased due to cellulose agglomeration especially in areas of high lignin content such as the secondary cell wall.
2.3 Solvent Selection

In determining the most effective solvent or solvent pairing for selective depolymerization, it is important to choose chemicals that discretely dissolve lignin and hemicellulose without dissolving cellulose. This is achievable because cellulose is physically insulated from chemical attack due to the protection provided by lignin, and to a lesser degree hemicellulose. Hemicellulose is also more susceptible to depolymerization than cellulose due to its non-crystalline nature especially in acidic conditions\(^6\). There are two mechanisms of selectively depolymerizing cellulosic material. The first is the Kamlet-Taft $\beta$ Parameter, a measure of a solvents ability to accept a hydrogen bond. Branching and bonding between the cellulosic biopolymers is achieved through hydrogen bonding. The $\beta$ Parameter needs to be less than or equal to 0.80 (unitless) in order for the solvent to be strong enough to remove the H bonds from the cellulose, but not damage the cellulose crystal structure. In addition to this, the size and shape of the nucleophile can play a critical role in the selectivity for dissolving these carbohydrates. For example, smaller molecular weight solvents with fewer substituents can penetrate deeper into the lignocellulosic chemistry relative to bulky nucleophiles. Based on these concepts, the choice of solvents for effectively selectively depolymerizing hemp was sodium chlorite (NaClO$_2$), and acetic acid (CH$_3$COOH). The specific mechanisms of depolymerization pertaining to the acid chlorite treatment was acid hydrolysis and oxidative cleavage of the polymer chains\(^9\). Figure 3 provides an animation of how the chemical pretreatment should interact with the cellulosic anatomy.

![EFFECT OF PRETREATMENT](image)

Figure 3. An animation of cellulosic material before and after the depolymerization pretreatment. The cellulose is left mostly intact while the lignin and hemicellulose have been selectively removed by a reduction in hydrogen bonding\(^{10}\).
3.0 Experimental Procedure

A standard operating procedure was developed in congruence with Environmental Health and Safety. Sodium chlorite is reactive, and acetic acid is flammable. Proper PPE such as splash-proof goggles, Neoprene with natural rubber blend gloves, and a fume hood were used through the entirety of the experiment. Chlorite and acetic acid depolymerization was conducted according to documented research\(^9\). First, 10 g of industrial hemp was ground in a coffee mill on 4 cycles on fine setting. The ground hemp was added to a 1 L Erlenmeyer flask. This was followed by 320 ml of MilliQ water, a 2 inch stir bar, 3 g of sodium chlorite (99.5% purity), and 1 ml of acetic acid (30% v/v). The flask was placed on a hotplate, and heated to 170°F. The contents were stirred for 3 hours under the fume hood. At the 1 and 2 hour intervals, the chlorite and acetic acid concentrations were administered back into the solution, but no additional water was added. At 3 hours, the flask was removed from heat, and allowed to cool to room temperature and vented under the fume hood. The contents of the flask were pored through a strainer into a labeled plastic waste container. The treated hemp was washed with 100 ml MilliQ water. The rinsate from the strainer was captured in a beaker and pH tested. Rinsing was continued until the pH was greater than or equal to 5. Weight of the wet sample was taken after rinsing. The sample was then placed in a 500 ml beaker, and allowed to dry in an oven at 130°F until the samples weight was constant.

![Image of hemp being processed](image)

Figure 4. The hemp sample should appear lighter after drying due to the removal of lignin - the main pigment of wood.

4.0 Results and Discussion

4.1 Scanning Electron Microscopy

Scanning electron microscopy was implemented to get a visual, qualitative assessment of the anatomical changes that should have been induced by the chemical pretreatment. All samples, control and treated, were gold sputtered prior to observing under the SEM to reduce charge buildup – a common remedy for nonconductive samples. The alternative to this option was to view the samples under low vacuum settings which fill the atmosphere with water to reduce the charge buildup. However, this method was ultimately decided against because the hemp samples would likely swell due to vapor absorption which could scue the size, and the sample’s degree of porosity relative to ambient vapor content. With this in mind, the
samples were viewed under an SEM FEI Quanta 200 at 15kV with a spot size of 4 on high vacuum settings. The exact pressure of the vacuum, and filament current were variable between samples. As hypothesized, the control hemp showed some inherent porosity as shown in Figure 5.

Figure 5. SEM image of control hemp sample shows inherent porosity as highlighted by the red circle. Fibrils are dense, and intact - a drastic difference from the treated samples.

The chemically treated samples showed a significant increase in porosity along the longitudinal fibril direction. This coincided with expected results from cited literature, as the secondary cell wall runs along the longitudinal direction of the cellulose fibrils. The secondary cell was the targeted area due to its high lignin concentration, and provided an area of cellulose agglomeration due to the structural integrity of the remaining cellulose. Figures 6 and 7 highlighted this phenomenon as the fibrils appear to be hallowed out along their longitudinal direction.

Figure 6. SEM image of depolymerized hemp highlights severe hallowing of the cellulose anatomy along the longitudinal direction. This was achieved by removing lignin from the secondary cell wall which induced agglomeration of the cellulose.
A cross-sectional area was exposed due to the coffee mill shear that further validates that the porosity did indeed run the length of the cellulose fibril. In addition to this, Figure 8 displayed another mechanism of increased porosity in the pitting of the fibril itself.
4.2 X-Ray Diffraction

X-ray Diffraction (XRD) was performed using a Siemens D5000 over a 2θ range 10° to 60°, a step size of 0.06° (2θ), and a step time of 0.6 s. The crystallinity index of the samples was calculated adhering to characteristic peak height method. Background signal was subtracted from the XRD pattern, and Equation 1 was used to calculate CI\textsubscript{XRD}. Figure 10 shows the intensity of the (200) peak at 2θ = 22.626° which represents both the amorphous and crystalline regions of cellulose while the height at 2θ = 18.058° corresponds to the amorphous cellulose only ($I_{110} = I_{AM}$).

$$CI_{XRD} (%) = \frac{I_{200} - I_{AM}}{I_{200}} \times 100$$

This method diffracts the amorphous material with the same intensity X-ray at 18.5° and 22.2°. The crystalline cellulose does not appear in the intensity at 18.5°.

Figure 9. XRD patterns of the fiberized hemp hurd before and after chemical pretreatment. The characteristic amorphous and cellulose peaks are indicated for calculating percent crystallinity.

The characteristic intensities and resulting crystallinity index was recorded in Table I. Intensities of both the amorphous and crystalline regions were smaller in scale, but the percent crystallinity of the cellulose structural unit was maintained at 63% after chemical treatment. This paralleled the qualitative assessment derived from the SEM images that displayed the congruency of the fibril orientation. As previously discussed, it was important to maintain crystal structure for the hollowing effect to be effective along the secondary cell walls.
Table I. XRD Pattern Intensities and Resulting Percent Crystallinity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{22}$</th>
<th>$I_{18}$</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Hurd</td>
<td>4586</td>
<td>2659</td>
<td>63.29%</td>
</tr>
<tr>
<td>Chemically Treated</td>
<td>1007</td>
<td>572</td>
<td>63.77%</td>
</tr>
</tbody>
</table>

4.3 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was conducted on a TA Instruments TGA 5500, and the data was analyzed using TA Universal Analysis. The thermal decomposition of the hemp samples was monitored from 20°C to 600°C at a 5°C per minute heating interval, and aluminum pans were used for sample holders. The samples weighed approximately 5 mg, and no inert purge gas was used. TGA was implemented to draw conclusions on the degree of depolymerized based on respective percent mass compositions of cellulose, hemicellulose, and lignin. Hemicellulose pyrolysis occurs over a range of 225°C to 325°C, cellulose from 325°C to 375°C, and lignin gradually over 250°C to 500°C. The resulting data is a one-step, three component model that required kinetics data regarding pyrolysis rates of the biopolymers for the specific chemistry of the wood in order to determine exact compositions. Kinetics data could not be found relating to the pyrolysis of hemp biopolymers, and the chemically treated samples could potentially have their own unique kinetics due to induced chemical changes. However, some general qualitative trends were derived from the overlaid TGA plot in Figure 10.

![TGA plot](image.png)

Figure 10. TGA plot of the control hemp sample designated by the dashed line, and the chemically treated sample shown as the full line.
The TGA sample was analyzed in reference to sources from literature in order to deduce trends regarding decomposition and depolymerization of the three main biopolymers. Cellulose showed higher resilience to thermal degradation relative to hemicellulose due to its crystalline structure. Cellulose undergoes three main reactions when heated: dehydration, oxidation, and depolymerization. Thermooxidation and dehydration occurred most frequently in the amorphous phases of the polysaccharides. Above 300°C the dominant degradation of cellulose was attributed to depolymerization. The decrease in weight percentage that occurred between 335°C and 360°C is the main region of cellulose decomposition which is evident due to the steep slope of mass loss over temperature. Both samples achieved approximately 95% weight loss. The chemically treated sample showed almost double the vapor content relative to the control sample, and could be due to prolonged drying times due to increased porosity. Table II provides qualitative trends that were observed from the TGA data.

Table II. Ranges of Cellulosic Material Decomposition Derived from TGA Data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degradation Range 1</th>
<th>Inflection Point</th>
<th>Degradation Range 2</th>
<th>Weight Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>240-335°C</td>
<td>335°C</td>
<td>335-450°C</td>
<td>94%</td>
</tr>
<tr>
<td>Chemically Treated</td>
<td>225-325°C</td>
<td>300°C</td>
<td>300°C-490°C</td>
<td>95%</td>
</tr>
</tbody>
</table>

| Mode       | Depolymerization of hemicellulose + degradation of lignin | Decomposition of cellulose + degradation of lignin | Degradation of lignin |

The decrease in degradation ranges, and the inflection point of cellulose decomposition is attributed to the anatomical changes induced during depolymerization. Cellulose lost an unquantified amount of thermal stability support from lignin and hemicellulose, so degradation began at a lower temperature. A similar explanation was used to describe the shift in Degradation Ranges 1 and 2. The removal of supporting and insulating structures caused an earlier onset of pyrolysis in hemicellulose and lignin. The gradual pyrolysis of lignin is evident in both samples as it is the most thermally stable polymer within the material.
4.4 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a common analytical chemistry technique for identifying functional groups in polymers by measuring covalent bond interactions. FTIR was conducted using a JASCO FT/IR-4600 over a wavenumber range from 500 cm\(^{-1}\) to 4000 cm\(^{-1}\) for a total of 24 scans. FTIR spectra were taken of the hemp before and after chemical treatment, and the data was overlaid in Figure 11.

![FTIR Spectra](image)

Figure 11. FTIR spectra of both the control and depolymerized samples. Characteristic functional group features of cellulose have been highlighted by the black boxes and descriptions. The most notable difference occurs around 3338 cm\(^{-1}\), the region associated with hydrogen bonding.

Fundamental functional group features were identified from the IR spectra. Common stretching characteristics and frequencies associated with cellulose, lignin, and hemicellulose from hemp have been compiled in Table III. Table III provided an exhaustive list of stretching frequencies common to cellulosic materials, but there were a few worth highlighting. The first was at 1729 cm\(^{-1}\) as this was indicative of stretching vibrations of unconjugated carbonyl groups found in hemicellulose. The depolymerized sample showed significant reduction in transmittance at this peak indicating a removal of the hemicellulose component. One peak that was not highlighted on Figure 11, but was still noted, was at approximately 1507 cm\(^{-1}\). The presence of this peak in both spectra indicated that lignin was present in both the control and treated samples, but to a lesser degree in the latter. Lignin is resistant to depolymerization due to strong C-C bonds, and other resilient functional groups such as aromatics. The region denoted by the C=C double bond region indicated the presence of aromatics, but also stretching associated with water vapor present within the cellulose matrix.
Table III. FTIR Frequencies of Functional Groups and Their Sources.

<table>
<thead>
<tr>
<th>WAVENUMBER (CM$^{-1}$)</th>
<th>VIBRATION OF FUNCTIONAL GROUP</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3362</td>
<td>OH Stretching</td>
<td>Polysaccharides</td>
</tr>
<tr>
<td>2902</td>
<td>C-H symmetrical stretch</td>
<td>Polysaccharides</td>
</tr>
<tr>
<td>1729</td>
<td>C=O unconjugated stretch</td>
<td>Hemicellulose</td>
</tr>
<tr>
<td>1633</td>
<td>OH (water)</td>
<td>Cellulose</td>
</tr>
<tr>
<td>1507</td>
<td>C=C symmetric stretch of aromatic ring</td>
<td>Lignin</td>
</tr>
<tr>
<td>1454</td>
<td>CH$_2$ bending</td>
<td>Lignin</td>
</tr>
<tr>
<td>1422</td>
<td>CH$_2$ bending</td>
<td>Cellulose</td>
</tr>
<tr>
<td>1373</td>
<td>CH bending</td>
<td>Cellulose</td>
</tr>
<tr>
<td>1320</td>
<td>CH$_2$ wagging</td>
<td>Crystalline Cellulose</td>
</tr>
<tr>
<td>1265</td>
<td>CO stretching</td>
<td>Lignin</td>
</tr>
<tr>
<td>1157</td>
<td>C-O-C asymmetric oxygen stretch</td>
<td>Cellulose</td>
</tr>
<tr>
<td>1028</td>
<td>C-C, C-OH, C-H ring and side group vibration</td>
<td>Hemicellulose, pectin</td>
</tr>
<tr>
<td>896</td>
<td>Glycosidic bond symmetric ring-stretching mode</td>
<td>Polysaccharides</td>
</tr>
</tbody>
</table>

The most significant takeaway from the FTIR spectra was the dramatic reduction in O-H stretching most associated with hydrogen bonding. This occurred in the broad and high intensity region at approximately 3362 cm$^{-1}$. This reduction in transmittance coincided with the removal of lignin and hemicellulose that was bound to the cellulose via H-bonds. Successful depolymerization was also expressed in the reduction of intensities of the treated samples in characteristic lignin stretches around 1507 cm$^{-1}$, and 1729 cm$^{-1}$ for hemicellulose. Future research should include using FTIR data to generate another mathematical model of percent crystallinity as an auxiliary method for the XRD data.
5.0 ASTM C518

The hemp hurd samples were tested for insulating performance (R-value) per ASTM C518 at RADCO Laboratories in Long Beach, CA. ASTM C518 is specifically designed for rigid batt insulation, so some error was introduced due to the nature of the fiberized hemp material. Figure 12 and 13 shows how the samples were formed into rigid structures to adhere to the mechanisms described per ASTM C518. Additionally, there was not enough material to fill a 12” x 12” x 2” sample shape; however, the ASTM does allow for an 8” x 8” x 2” sample if the boundaries are properly insulated. Both the control and treated hemp samples were cast in the form of the latter dimensions using a mesh frame, and properly insulated with expanded polystyrene.

Figure 12. The control hemp sample was fixed into a rigid shape to simulate batt insulation. The dimensions were 8” x 8” x 2”.

The thermal conductivity machine at RADCO was designed for 12” x 12” samples, so additional insulation was placed around the missing 4” of sample to simulate the square foot design. The supplementary batt insulation was observable around the perimeter of the sample in Figure 13.
A full report generated by RADCO can be viewed in the Appendix. Key information regarding the results of ASTM C518 for the two samples was compiled in Table IV. Exact R values (per inch) could not be derived due to error in the thickness measurements. The auxiliary batt insulation played a role in this source of error for thickness, and for thermal conductivity and resistance. ASTM C518 is specifically designed for rigid foam insulators, so the extent to which the results were interpreted was limited. Remedies for this were addressed in the Future Research section of this report, and the resolution is in adhering to ASTM C739 which is specifically designed for cellulose loose fill insulation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (pcf)</th>
<th>Thermal Conductivity k (BTU.in)/(Hr.ft².°F)</th>
<th>Thermal Resistance R (Hr.ft².°F)/BTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Hemp</td>
<td>8.28</td>
<td>0.419</td>
<td>5.79</td>
</tr>
<tr>
<td>Treated Hemp</td>
<td>5.84</td>
<td>0.396</td>
<td>6.15</td>
</tr>
</tbody>
</table>

The reduction in density of the depolymerized sample relative to the control hemp paralleled the hypothesis of increasing porosity, which is synonymous with decreasing density. The industry standard density for cellulose insulation is 3.5 pounds per cubic foot (pcf), and has an R-value per inch of approximately 3.4-3.8 (Hr.ft².°F)/BTU.in\(^\text{13}\). Fiberglass batt, the industry standard, has an R-value per inch that ranges from 3.2 to 3.8 (Hr.ft².°F)/BTU.in. It has been reported by the United States Department of Energy that cellulose insulation derived from hemp (at the proper density) has an R-value of 3.5 per inch. This is encouraging, as any improvement on the inherent insulating properties of the hemp will further lead to competitive insulating performance relative to fiberglass and other cellulose alternatives. A 30% decrease in density due to depolymerization resulted in a boost in insulating performance, and will further
be enhanced when applied to properly fiberized hemp cellulose. Further reduction in density can be achieved using a mechanical fiberizer, or hammermill, and will be a focus in future research.

6.0 Conclusions

Cannabis sativa, commonly referred to as industrial hemp, has potential to be a source of cellulose for blow-in insulation for residential and commercial buildings. The scope of this study was to gauge the effectiveness of increasing thermal insulation performance by introducing porosity to the anatomy of the cellulosic material via selective depolymerization. This was successfully achieved by implementing a sodium chlorite and acetic acid catalyst chemical pretreatment. The degree to which the material was selectively depolymerized could not be definitively evaluated through TGA. However, qualitative assessments from SEM images and FTIR spectra provided sufficient evidence that confirm depolymerization of the cellulosic anatomy was achieved. Additionally, the percent crystallinity of the cellulose was maintained at 63% which allowed for the maximum surface area of induced porosity. The cumulation of qualitative data was further validated per ASTM C518, which showed an increase in thermal insulating performance from untreated hemp at 2.4 (Hr.ft².°F)/BTU, and selectively depolymerized hemp at 2.7 (Hr.ft².°F)/BTU. The report generated by RADCO had a different thickness value for both samples than what was measured on site, so conclusions regarding the exact change in R-value must be considered with this and other sources of error in mind. The chemical treatment was effective in increasing thermal insulation, and provides opportunity for optimization in future endeavors.

6.1 Future Research

Future research goals have been highlighted in the results and discussion section of the report. Continued research will be conducted this summer with generous funding from VentureWell E Team cohorts, and through the CIE HotHouse Accelerator program. The first area that will be addressed is reducing the treated samples density from 5.84 pcf (pounds/ft³) to approximately 3.5 pcf. This can be achieved by introducing the material to a mechanical fiberizer, or hammermill – two industry standards for cellulose insulation. Next, a method will be derived to gauge the degree of depolymerization in order to optimize this with respect to the insulating metric (R-value). There are two routes for achieving this: acid dissolution and analysis, or continued TGA analysis with the appropriate kinetics information. This will be crucial in moving forward with a fully optimized chemical treatment that can both save money, and increase performance. Additionally, an optimized percentage of hemp fiber may be introduced to the pure hemp hurd sample to increase insulating performance. Hemp hurd was the initial choice due to its cost competitive nature, but hemp fiber has been known to have increased thermal insulation relative to the hurd due to its fibrous nature. However, hemp fiber is in high demand as a candidate to compete with the cotton industry. Future research will be conducted to find if adding an optimized weight fraction of fiber to the hurd can improve R-value without a significant cost increase. R-value will be tested using experimental methods related to ASTM C518 until a fully optimized treated sample is achieved. Ideas for this include a steady state heat source with insulated boundaries and a mathematical model for determining heat transfer. This sample will then be subjected to ASTM C739; a test specifically designed for cellulose insulation. One sample conducted for ASTM C739 costs approximately $3,000, so this will be pursued after optimization. Finally, alternative solvent options will be explored further. Most notably, the implementation of cutting edge ionic liquids have shown promise in achieving selective depolymerization on cellulosic material, and are cost effective and can be regenerated for repeated uses.
7.0 References


8.0 Appendix
RADCO TEST REPORT
Test Report No. RAD-5952
Project No. C3823A
Lab No. TL-3987

Industrial Hemp and Chemically Treated Industrial Hemp
Evaluated For Thermal Resistance in Accordance with ASTM C518-15

Prepared for

CAL POLY CORPORATION
Building 15
San Luis Obispo, CA 93407

by

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Reviewed by:
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Principal Engineer

Issued: May 23, 2017

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4.0 PHOTOGRAPHS ........................................................ 3
1.0 INTRODUCTION

At the request of Cal Poly Corporation, RADCO conducted thermal resistance tests on samples of Industrial Hemp and Chemically Treated Industrial Hemp material.

2.0 MATERIAL

One (1) small container of Industrial Hemp material and one (1) small container of Chemically Treated Hemp material were received at RADCO’s Long Beach, CA test facility on May 19, 2017.

2.1 CONDITIONING

Samples were conditioned for a period of not less than 40 hours at a temperature of 73.4 ± 4°F (23 ± 2°C) and a relative humidity of 50 ± 5% unless otherwise specified in the individual standards.

3.0 ASTM STANDARD C518-15, THERMAL TRANSMISSION PROPERTIES BY MEANS OF THE HEAT FLOW METER APPARATUS

3.1 TEST EQUIPMENT

1. Steel rule graduated to 1mm
2. Sartorius Model GP3202 electronic digital scale
3. Holometrix Micromek (Metrisa Company) Lambda 2000 Series heat flow meter thermal conductivity instrument

3.2 TEST METHOD

Testing was conducted in accordance with ASTM Standard C518. One nominal (1) 8.5" x 8.5" (217 mm x 217 mm) open face container was used to test each material. The container’s sides and bottom were made of a screen mesh to allow the insulation to have contact with both thermal plates within the thermal conductivity machine. The top part of the container did not have a screen. Each material was tested at a mean temperature of 75° ± 2°F (23.9 ± 1.1°C). The actual specimen thickness was determined in the heat flow meter apparatus. The specimens were placed at the center of the plate and tested in the 4" x 4" metering area of the apparatus. Expanded Polystyrene insulation was placed in the empty spaces between the four specimen sides and the apparatus. The recorded data and the results are shown in the following table.
Specimen ID. |Industrial Hemp |Chemically Treated Hemp |
-------------|-----------------|------------------------|
Date of Test: |5/19/17          |5/23/17                |
Hot plate temperature °F: |93.63            |94.58                  |
Cold plate temperature °F: |52.75            |54.55                  |
Mean temperature during test °F: |73.19            |74.56                  |
Temperature gradient during test °F: |40.88            |40.04                  |
Specimen thickness as tested (in): |2.43             |2.43                   |
Duration of measurement portion of test (hrs:min:sec): |02:34:22         |02:53:17               |
Final specimen mass (wt.) after test (gms): |379              |266.96                 |
Thermal conductivity "k": (BTU.in)/(Hr.ft2. °F) |0.419            |0.396                  |
Thermal resistance "R" per specimen thickness: (Hr.ft2. °F)/BTU |5.79             |6.15                   |
Density of Specimen (pcf) |8.28             |5.84                   |

Note 1: Last heat flow meter calibration date: 5/19/17
Note 2: Type of calibration material used: fiberglass

*****END OF REPORT*****
4.0 PHOTOGRAPHS

Industrial Hemp Material in Container

Industrial Hemp Container inside Thermal Conductivity Machine

Chemically Treated Industrial Hemp

Chemically Treated Hemp inside Machine
RADCO TEST REPORT

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