Comparative kinetic study of the thermal decomposition of nanocellulose produced by H₂SO₄ hydrolysis, Tempo, and AVAP processes

Jamila Shakira Marshall
Clark Atlanta University

Follow this and additional works at: http://digitalcommons.auctr.edu/dissertations
Part of the Chemistry Commons

Recommended Citation
http://digitalcommons.auctr.edu/dissertations/3114

This Thesis is brought to you for free and open access by DigitalCommons@Robert W. Woodruff Library, Atlanta University Center. It has been accepted for inclusion in ETD Collection for AUC Robert W. Woodruff Library by an authorized editor of DigitalCommons@Robert W. Woodruff Library, Atlanta University Center. For more information, please contact cwiseman@auctr.edu.
ABSTRACT

DEPARTMENT OF CHEMISTRY

MARSHALL, JAMILA B.S. UNIVERSITY OF THE WEST INDIES, CAVE HILL CAMPUS, 2010

COMPARATIVE KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NANOCELLULOSE PRODUCED BY H₂SO₄ HYDROLYSIS, TEMPO, AND AVAP® PROCESSES

Committee Chair: Eric A. Mintz, Ph.D.

Dissertation dated July 2015

Cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) are of great interest as reinforcing phases for polymer matrix composites; however, CNCs and CNFs prepared by the sulfuric acid hydrolysis and TEMPO process, respectively, have been reported to lack the thermal stability necessary for incorporation in many polymer systems. We have compared the thermal stability of CNCs and CNFs prepared by the sulfuric acid hydrolysis, TEMPO, and AVAP® processes and the corresponding starting materials by thermogravimetric analysis (TGA). We found that the AVAP® process does not appreciably reduce the thermal stability of the nanocellulose relative to the cellulose in the starting material. Sulfuric acid hydrolysis and TEMPO oxidation of cellulose gives CNCs and CNFs, respectively, that have a much lower thermal stability than the cellulose from which they were prepared.

X-Ray Diffraction (XRD) analysis was used to examine the degree of crystallinity and crystallite size of the nanomaterials and corresponding starting materials; however,
the degree of crystallinity determined by XRD showed no correlation with the thermal stability of the nanocellulose materials.
COMPARATIVE KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NANOCELLULOSE PRODUCED BY H₂SO₄ HYDROLYSIS, TEMPO, AND AVAP® PROCESSES

A THESIS

SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF CHEMISTRY

BY

JAMILA SHAKIRA MARSHALL

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

JULY 2015
ACKNOWLEDGEMENTS

I first thank God for the strength to persevere through this process. I would also like to thank Clark Atlanta University for the opportunity to pursue this degree. A special and heartfelt thank you is extended to my advisor, mentor, and friend Dr. Mintz for answering my many questions and guiding me through this process, as well as for affording me the opportunity to work with the Mintz group. I thank my committee members Dr. Parker and Dr. Tandabany for their guidance and advice. I am also grateful to my colleagues Ms. V. Sorsor, Mr. L. Cross, Mr. W. Simmons, and Mr. S. Golafale for their support and assistance.

I would like to thank Dr. G. Schueneman of USDA Forest Products Laboratory and Dr. K. Nelson of American Process Inc. for their contributions to this research, as well as USDA Forest Products Laboratory, Grants 10-JV-11111104-066, 11-JV-1111129-117, 14-JV-1111129-020, and 15-JV-11111129-30 for financial support.

I thank my family and friends - especially my siblings and parents - who were constant providers of advice and a source of calm through my many stressful moments. Last but by no means least; I would like to thank my husband, Michael Roberts, for his unwavering love, support, advice and the level-headed rationality and peace which he brings to every area of my life. I am truly thankful to all.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ iii

LIST OF FIGURES .................................................................................................................... v

LIST OF TABLES ....................................................................................................................... vi

LIST OF ABBREVIATIONS ....................................................................................................... vii

CHAPTER

1. INTRODUCTION ................................................................................................................. 1

   1.1. Cellulose and Nanocellulose ..................................................................................... 1

   1.2. Thermal Analysis ....................................................................................................... 7

   1.3. Crystallinity of Cellulose ........................................................................................... 12

2. EXPERIMENTAL METHODS ............................................................................................. 16

   2.1. Materials .................................................................................................................... 16

   2.2. Calcium, Sodium, and Sulfur analyses of CNCs, CNFs, L-CNCs and L-CNFs .......... 17

      2.3.1. Instrumentation – Thermogravimetric Analysis (TGA) ..................................... 17

      2.3.2. Instrumentation – X-ray Diffraction (XRD) Analysis ........................................ 18

3. RESULTS AND DISCUSSION ........................................................................................... 19

   3.1. Introduction ............................................................................................................... 19

   3.2. Thermogravimetric Analysis ..................................................................................... 20

   3.3. Model-Fitting and Model-Free Methods .................................................................. 24

   3.4. Calculation of Kinetic Parameters .......................................................................... 38

   3.5. Projection of Half-life vs. Temperature .................................................................. 42

   3.6. Calcium, Sodium, and Sulfur Analyses of CNCs, CNFs, L-CNCs and L-CNFs ......... 45
3.7. X-ray diffraction Analysis ................................................................. 47
4. CONCLUSION .......................................................................................... 51

APPENDIX

A. Representative graphs showing the application of Kissinger model-free methods to nanocelluloic materials............................................................... 53
B. Representative graphs showing reproducibility tests ............................... 61

REFERENCES ................................................................................................ 63
LIST OF FIGURES

Figure 1. Molecular structure of cellulose ......................................................... 2

Figure 2. Flow diagram depicting the AVAP® process ......................................... 6

Figure 3. XRD diffractogram illustrating the crystalline ($I_{002}$) and amorphous ($I_{AM}$) heights used to calculate the crystallinity index .................................................. 14

Figure 4. Thermogram showing the weight % vs. T and the derivative of percent weight loss with respect to temperature curves obtained for the eucalyptus dissolving pulp used for sulfuric acid hydrolysis CNCs at a ramp rate of 10 °C/min under N₂ ................................................................................................................. 21

Figure 5. TGA curves showing weight loss vs. temperature for AVAP® CNCs and CNFs, and FPL produced CNCs, and TEMPO CNFs at 10 °C/min under N₂ ..................... 22

Figure 6. TGA curves showing the comparison of L-CNCs and CNCs produced by the AVAP® process heated at 10 °C/min under N₂ ...................................................... 23

Figure 7. TGA curves showing the comparison of L-CNFs and CNFs produced by the AVAP® process heated at 10 °C/min under N₂ ...................................................... 24

Figure 8. Representative graphs showing the application of nucleation model-fitting methods, equations 1 – 6 as in Table 3, to data obtained from FPL CNCs ...................... 27

Figure 9. Representative graphs showing the application of diffusion model-fitting methods, equations 7 and 8 in Table 3, to data obtained from FPL CNCs ...................... 28

Figure 10. Representative graphs showing the application of reaction order and geometrical contraction model-fitting methods, equations 9 – 12 in Table 3, to data obtained from FPL CNCs .............................................................................................. 29

Figure 11. Representative graph showing the application of the Coats-Redfern method to AVAP® CNCs ............................................................................................... 32

Figure 12. Representative graph showing the application of the O-F-W method to AVAP® CNCs ............................................................................................... 33
Figure 13. Representative graph showing the application of the Friedman method to AVAD® CNCs ................................................................. 34

Figure 14. Representative graphs showing the activation energies calculated using the Coats-Redfern method vs. the degree of conversion, α, for AVAD® CNCs, CNF, L-CNCs, L-CNFS and FPL CNCs and CNFs .................................................................................................................................................. 35

Figure 15. Representative DTG curves for the dissolving pulp used to prepare CNCs by sulfuric acid hydrolysis ........................................................................................................................................................................... 37

Figure 16. Representative graph showing the application of the Snyder modified Kissinger model-free method to the dissolving pulp used to prepare CNCs by sulfuric acid hydrolysis ........................................................................................................................................................................... 38

Figure 17. Comparison of projected half-lives for API and FPL CNCs as a function of temperature ......................................................................................................................................................... 43

Figure 18. Comparison of projected half-lives for API and FPL CNFs as a function of temperature ............................................................................................................................................................. 44

Figure 19. Comparison of projected half-lives for two batches FPL CNFs with 0.65 mmol/g Na and 1.3 mmol/g Na as a function of temperature ......................................................................................................................... 45

Figure 20. Graph showing the Ca, Na, and S content of the CNCs, CNFs, L-CNCs and L-CNFS investigated ........................................................................................................................................................................... 46

Figure 21. XRD diffractogram obtained for the dissolving pulp used to prepare CNCs by sulfuric acid hydrolysis ......................................................................................................................................................... 47

Figure 22. XRD diffractogram obtained for the FPL dissolving pulp used in the production of CNCs and adjusted by HighScore ............................................................................................................................................................. 48
LIST OF TABLES

Table 1. Mathematical methods for model-free treatment of weight loss vs. temperature and time for TGA data ................................................................. 12

Table 2. Results of the Elemental Analysis of Materials ........................................... 17

Table 3. Solid state reaction models (mathematical functions) for model-fitting of weight loss vs. temperature of TGA data ......................................................... 26

Table 4. Kinetic Parameters calculated for AVAP® Samples using the Kissinger Method modified by Snyder et al. ................................................................. 39

Table 5. Kinetic parameters calculated for CNCs produced by sulfuric acid hydrolysis and corresponding source material using the Snyder modification of the Kissinger model ................................................................. 40

Table 6. Kinetic parameters calculated for CNFs produced by the TEMPO process and the corresponding starting material using the Snyder modification of the Kissinger model ................................................................. 41

Table 7. Degrees of crystallinity calculated for the nanocellulosic materials .......... 49

Table 8. Crystallite sizes of nanocellulosic materials as calculated using the Scherrer method ................................................................. 50
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td>API</td>
<td>American Process Inc.</td>
</tr>
<tr>
<td>AVAP®</td>
<td>American Value Added Pulping</td>
</tr>
<tr>
<td>BC</td>
<td>Bacterial nanocellulose</td>
</tr>
<tr>
<td>CNCs</td>
<td>Cellulose nanocrystals</td>
</tr>
<tr>
<td>CNFs</td>
<td>Cellulose nanofibers</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of Polymerization</td>
</tr>
<tr>
<td>DTG</td>
<td>First derivative of the thermogravimetric analysis curve</td>
</tr>
<tr>
<td>Ea</td>
<td>Activation Energy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half-maximum</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>L-CNCs</td>
<td>Lignin-coated cellulose nanocrystals</td>
</tr>
<tr>
<td>L-CNFs</td>
<td>Lignin-coated cellulose nanofibers</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocellulose</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OFW</td>
<td>Ozawa-Flynn-Wall</td>
</tr>
<tr>
<td>SAH</td>
<td>Sulfuric Acid Hydrolysis</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethylpiperidine-1-oxyl</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
</tbody>
</table>
1.1 Cellulose and Nanocellulose

In our society, there is currently a significant movement to utilize materials and practices which cause minimal damage to the environment and are commonly termed "green" materials. Materials that meet these requirements are renewable, non-toxic, and biodegradable. One material that meets these requirements is cellulose. Cellulose is one of the most abundant materials on the planet and consists of repeating glucose (d-glucopyranose) units joined by β-1-4 linkages as shown in Figure 1. It has a degree of polymerization (DP) of 10,000 – 20,000. The degree of polymerization refers to the average number of repeat units in the polymer. Cellulose is usually found in nature as an assemblage of fibers consisting of approximately thirty six individual cellulose chains forming protofibrils, which then combine to form microfibrils and further assemble as cellulose fibers. Cellulose is essential for the structural integrity of plant cell walls and is water insoluble.
Figure 1. Molecular structure of cellulose.\textsuperscript{5}

It has been experimentally found that cellulose exists in four different allomorphs which may be interconverted using thermal and chemical methods. These forms have been named I (I\textsubscript{a} and I\textsubscript{b}), II, III and IV; however, structure of the various allomorphs have not been fully determined.\textsuperscript{6} Cellulose I is commonly referred to as native cellulose. Cellulose II is not commonly found in nature but is more stable than cellulose I and is manufactured from cellulose by regeneration or mercerization. Regeneration entails dissolution of cellulose in a solvent followed by recrystallization while mercerization is the swelling of cellulose in aqueous sodium hydroxide followed by recrystallization.\textsuperscript{7} Cellulose III was produced via swelling of crystalline cellulose ammonia complexes of cellulose I or II.\textsuperscript{8} Cellulose IV has been obtained from cellulose III by treatment with glycerol at elevated temperatures.\textsuperscript{9}

Cellulose may be obtained from a variety of sources which include algae, bacterial sources, wood, plants, amoebas and tunicates. Algal sources include several species, such as \textit{Boergesenia}, in which cellulose microfibrils are produced in the cell walls.\textsuperscript{6} Bacterial cellulose is generally synthesized by the \textit{Gluconoacetobacter xylinius}
family of bacteria which secrete cellulose microfibrils. This secretion is gelatinous and composed of over 95% water along with cellulose microfibrils. It has been suggested that it serves as a protective mechanism against other microorganisms and/or ultraviolet light. Wood is also used as a source of cellulose and is advantageous due to its abundance and preexisting facilities, paper mills, for its processing. Plant sources are also abundant and processing is easily facilitated by existing infrastructure. These sources include cotton, flax and wheat straw.

Tunicates are the primary animal source known for producing cellulose. Tunicates are marine animals which possess a thick, leathery mantle which can be used as a cellulose source after the animals have reached maturity. The cellulose microfibrils are embedded in a protein matrix within the mantle and have been extracted by first isolating the mantle of the animal and then isolating the individual fibrils of cellulose by removing the protein matrix. Cellulosic nanomaterials may be obtained from the mantle by acid hydrolysis, enzymatic hydrolysis, or mechanical treatment. The class of tunicates most often used for this purpose are “sea squirts” (Ascidiae).6

Cellulose is viewed as a natural alternative to petroleum based and mined products. Specifically, nanoparticles from this polymer, termed nanocellulose (NC), are favored as potential polymer additives due to their good mechanical and optical properties, strengthening effect when incorporated into polymers, high aspect ratio (length to diameter), and low coefficient of thermal expansion.11 As such, nanocellulose has found applications in the manufacture of many products including high performance fillers for paper, cement, plastics, paints and packaging, as well as a viscosity modifier
for oil-drilling fluids and cosmetics. NC may also be used in barrier, antimicrobial and transparent films, biomedical implants, and pharmaceuticals.

Nanocellulosic materials have also been divided into cellulose nanofibers (CNFs), cellulose nanocrystals (CNCs), and bacterial nanocellulose (BNC). These terms have been widely used for varying materials and standardizations of such terms are currently being drafted by the International Organization for Standardization (ISO).

Cellulose nanofibers are bundles of stretched cellulose chains which are entangled, flexible and approximately 5 - 60 nm in diameter and several micrometers long. Cellulose nanofibers incorporate alternating crystalline and amorphous domains (regions without a defined crystalline structure). Cellulose nanocrystals are crystalline, elongated and rod-like with limited flexibility. These are the smallest structural units in plant fibers. CNCs do not contain amorphous regions. The morphology of CNCs is dependent on the source material, due to varying biosynthetic processes used by plants and animals. For example, the nanocrystals from wood are approximately 3 - 5 nm in width and 100 - 200 nm in length while those from tunicates are approximately 10 - 20 nm in width and 500 - 2000 nm long.

Nanocellulose is primarily produced by the sulfuric acid hydrolysis of wood pulp, TEMPO oxidation of wood pulp, AVA® processing of wood pulp, wood chips, or harvest residues, or by enzymatic processing. The USDA Forest Products Laboratory (FPL) has built a pilot plant to provide U.S. universities and companies with samples of cellulose nanomaterials to investigate. FPL utilizes 64% sulfuric acid to hydrolyze dissolving pulp to produce CNCs by dissolving the amorphous regions without disrupting
the crystalline regions. The CNCs were then purified using two stages of dilution and settling to remove salts and sugars. The CNCs produced contained sulfonic acid groups which under basic conditions led to the formation of a stable suspensions. Water was then removed using membrane filtration and the resulting CNCs were freeze-dried.\textsuperscript{12}

The FPL prepared CNFs by selective conversion of hydroxyl groups present on the surfaces of plant celluloses by catalytic oxidative pretreatment using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals in water. This resulted in the selective conversion of C\textsubscript{6} primary hydroxyl cellulose groups to carboxylate groups via the C\textsubscript{6} aldehyde, using sodium hypochlorite or sodium chlorite as the oxidants.\textsuperscript{13} Sodium hypochlorite (NaClO) was the oxidant used to produce CNFs with a sodium concentration of 1.30 mmol/g and sodium chlorite (NaClO\textsubscript{2}) was used to produce CNFs with a sodium concentration of 0.65 mmol/g.\textsuperscript{13} After the TEMPO-mediated oxidation, batches were dispersed in water and homogenized using high pressure. The CNFs were freeze-dried but other drying techniques which include air-drying, oven-drying, spray-drying or supercritical drying have also been used to isolate dry CNFs.\textsuperscript{1}

The AVAP\textsuperscript{®} process has been developed by American Process, Inc. (API) of Atlanta, GA to use plant and wood sources as staring materials to produce CNCs and CNFs.\textsuperscript{10} Samples of AVAP\textsuperscript{®} CNCs and CNFs have been made available to a very small number of universities for study. In the AVAP\textsuperscript{®} process, biomass is chemically pretreated using sulfur dioxide and ethanol to remove lignin, hemicelluloses, and amorphous regions of the cellulose. The sulfur dioxide frees the cellulose and hemicelluloses from the lignin while ethanol serves as the process solvent. The
recovered lignin is burned to serve as an energy source for the process with the goal of achieving energy self-sufficiency. The nanocellulose material produced is dependent on the time and temperature of the pretreatment step giving either CNFs or CNCs as desired. The remaining dissolved lignin and sugars are then removed from the chemically fibrillated cellulose pulp by washing. The pulp is then bleached to obtain pure cellulose. Minimal mechanical energy is then applied to obtain the individual particles of nanocellulose. Samples are then freeze-dried or spray-dried. A flow diagram summarizing this process is shown in Figure 2.

![Figure 2. Flow diagram depicting the AVAP® process.](image)

Of the methods used to prepare cellulose nanomaterials, the enzymatic processing is the least standardized. According to Fan et al., the characteristics of cellulose which
influence suitability to degradation using enzymatic methods include the "degree of water swelling, the crystallinity, the molecular arrangement, the content of associated material and the capillary structure of cellulose." The mechanism of this hydrolysis is not yet fully understood and may vary depending on the enzyme used. One family of enzymes that has been used is cellulase. This term refers to any of a number of enzymes which may be used in the breakdown of cellulose.

1.2 Thermal Analysis

Thermal analysis describes a series of techniques where a property, such as weight loss or heat flow, of a given material is monitored as a function of time and temperature, usually using a temperature program. It has been reported that nanocellulose undergoes thermal degradation with an onset of degradation between 200 and 300 °C which was dependent on the source of the material analyzed, heating rate, and the degree of surface modification. In some solid phase reactions chemical and physical changes occur preferentially at the surface of the crystals or where the reactant and product phases directly contacted each other.

Kinetic studies have been used to analyze and predict the behavior of chemically reacting systems under varied conditions. Important information such as durability, heterogeneity, structural elements, constitution, "metastable or polymorphic states of a compound, physical application", and its limitations have been determined by thermal analysis. Kinetic studies have been used to determine the extent of conversion of reactant or formation of product or products over the course of a reaction. The effect of
temperature on this rate has also been studied. Kinetic parameters which have been determined include the rate constant, activation energy, and the frequency factor or pre-exponential factor, A, for a reaction. The activation energy refers to the energy requirement in order for the reaction to occur successfully. The frequency factor, A, refers to the prevalence with which the reactant is ideally positioned for successful interaction for conversion to product.

According to Brown and Galway, the formulation of rate equations must take into consideration the following factors which may influence the reactions of solids: Firstly, the bond redistribution step(s) which occurred at the reaction interface, termed the chemical reaction. Secondly, the kinetic behavior may be influenced by the reaction geometry of the system. That is, the variations in the area of reaction interface due to the changes in geometry as the reaction proceeds. Finally, the rate of product formation may also be influenced by the rate of diffusion of reactants to or from the reaction interface.

Thermal decomposition kinetics has been studied by thermogravimetric analysis (TGA). This technique measures weight loss as a function of time and temperature, and has been used to study the thermal stability of cellulose. This technique provides an experimental curve of weight vs. temperature and time from which the first derivative (DTG) can be determined. Analysis of data can then be carried out via model-fitting or model-free isoconversional methods in order to determine the kinetic parameters, effect of temperature on the samples, and the relevance of theoretical thermal decomposition mechanisms. Model-fitted or nth order kinetics use a single dynamic measurement and multiple linear regression as a function of degree of reaction, \( \alpha \), for the calculation of
kinetic parameters (activation energy, pre-exponential factor, and rate constant). Model-free isoconversional methods use multiple dynamic measurements and multiple heating rates in order to calculate kinetic parameters. There has been a debate in the scientific literature as to which method is superior. Some suggested that model-free methods may be advantageous as no reaction mechanism assumption is required and complex, multistep thermal processes may be tackled. However, others have argued that the isoconversional principle is "fundamentally inapplicable to reaction networks having competing reactions" and may be a poor technique for reactions where conversion was incomplete. Thus, it is useful to study and compare both methods in order to make a determination on the validity and applicability of each to a particular system.

Three types of models have been used to analyze the model-fitted or n\textsuperscript{th} order kinetics using TGA. These models depend on the extent of the reaction, $\alpha$, as determined from thermal analysis. Models that have been utilized include nucleation, for example the power law and Avrami-Erofeev models, diffusion such as Janders and one-dimensional diffusion models, and reaction order and geometrical contraction. Geometrical contraction models include, for example, the contracting cylinder and contracting sphere models.

Nucleation models rely on the principle of nucleation which is defined as the "initial establishment of a new and discrete product particle within the solid reactant". It involves a material that has either recrystallized or reacted to give a product phase by a chemical transformation of one or more component species. The power law model, the simplest kinetic representation of this concept, is based on the assumption that the
surfaces of the solid grow at an unrestricted and constant rate through the formation of
growth nuclei in several dimensions. This was generally expressed as $a^{1/n} = kt$ where $n$
represents the number of dimensions of growth of nuclei, $k$ is the rate constant and $t$ is
time.\textsuperscript{18} This concept was further expanded by Avrami who assumed that nuclei would
grow in the absence of overlap and thus increased the value of extent of reaction, $a$. As
such, the Avrami-Erofeev equation was developed with the integral form $[-\ln(1 -
a)]^{1/n} = kt$, where $n$ represents the number of dimensions of nuclei growth on the basis
of the nucleation rate law.\textsuperscript{23}

Diffusion models were developed for solid state reactions where the product
formed was also a solid and the reaction proceeds by transport across a barrier, or in
instances where the rate of degradation of the solid was controlled by diffusion of a
volatile product from the reactants.\textsuperscript{18} In reactions of this type, the rate at which product
was formed was proportional to the thickness of the product barrier layer. In the simplest
case, the rate equation corresponds to an infinite flat plane and as such only one
dimension was considered.\textsuperscript{23} This one-dimensional diffusion model has the form
$\alpha^2 = kt$ where $k$ is a rate constant and $t =$ time. Janders expanded this equation to
develop a model of the form $\left[1 - (1 - \alpha)^{1/3}\right]^2 = k'$, where $t =$ time and $k' = k/R^2$ ($R =$
radius of a theoretical spherical particle).\textsuperscript{23}

Reaction order and geometrical contraction models have also been developed to
describe solid state reactions. Mampel first and second order models have been
employed where reaction order and the reaction rate are proportional to the concentration
of remaining reactant raised to the power of the assumed order. The first order model has
the form, \( \ln(1 - \alpha) = kt \) and the second order model was formulated as \( (1 - \alpha) - 1 = kt \). Geometrical contraction models were "based on an initial rapid dense
nucleation across all, or some specific, crystal faces". It was thought that the progress
of the reaction interface was the primary factor determining the rate of reactant
degradation. The shape of the model assumed, for example, cylinder or sphere was
determined by the shape of the crystal under examination. The contracting cylinder and
contracting sphere models were of the forms \( 1 - (1 - \alpha)^{1/2} = kt \) and \( 1 - (1 - \alpha)^{1/3} =
kt \), respectively.

Kissinger proposed that the variation in peaks obtained from differential thermal
analysis, derivative of the TGA curve, as a function of heating rate could be used to
determine the order and activation energy of a reaction. When the data obtained were
plotted as \( \ln \left( \frac{\beta}{T_m^2} \right) \) vs. \( \frac{1}{T_m} \), where \( \beta \) is the heating rate and \( T_m \) is the maximum of the
derivative of weight loss with respect to temperature, straight lines were obtained with
slope \( = \frac{-E_a}{R} \) and intercept \( = \ln \left( \frac{A R}{E_a} \right) \) where \( E_a \) is the activation energy, \( R \) is the gas
constant, and \( A \) is the pre-exponential factor. Kissinger developed this method to study
pure samples. Snyder et al. showed that this method could be modified to allow the study
of multi component biological systems including small biochemical species, biopolymers
and bacteria. This modification was developed based on the assumption that the
biological components of any given sample, biopolymers or biochemical, under analysis
do not interact, thereby allowing for the determination of kinetic parameters. It was also
assumed that the thermal degradation of these materials proceeded independently and simultaneously. The third assumption was that each of the maxima obtained experimentally from the negative derivatives of the TGA curves could be attributed to distinct reaction pathways. The final assumption was that each of these distinct reactions proceeded via first order kinetics. The Coats-Redfern, Friedman, and Ozawa-Flynn-Wall models that have been developed for the model-free kinetic analysis of TGA data are given in Table 1.

Table 1. Mathematical methods for model-free treatment of weight loss vs. temperature and time for TGA data

<table>
<thead>
<tr>
<th>Method</th>
<th>Plot*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coats-Redfern (Modified)</td>
<td>$\ln \left( \frac{\beta}{T^2} \right)$ vs. $1/T$</td>
</tr>
<tr>
<td>Friedman</td>
<td>$\ln \left[ \beta(T_m) \right]$ vs. $1/T_m$</td>
</tr>
<tr>
<td>Ozawa-Flynn-Wall</td>
<td>$\log \beta$ vs. $1/T$</td>
</tr>
<tr>
<td>Kissinger</td>
<td>$\ln \left( \frac{\beta}{T_m^2} \right)$ vs. $1/T_m$</td>
</tr>
</tbody>
</table>

*\(\beta\) is the heating rate, \(T\) is the temperature in Kelvin, \(T_m\) is the Kelvin temperature value of the maximum for the derivative of mass loss vs. temperature curve.

1.3 Crystallinity of Cellulose

The crystalline portion of cellulosic materials is dependent on the source of the cellulose as well as the methods used for its extraction. The crystallinity index (CrI), a parameter used to express the degree of crystallinity, may be determined using various
methods which include X-ray diffraction (XRD), infrared (IR) spectroscopy, Raman spectroscopy, and solid-state $^{13}$C nuclear magnetic resonance (NMR).\textsuperscript{28}

The degree of crystallinity may be obtained from XRD diffractograms using several techniques. One such method as described by the ISO uses the height of the peak at a diffraction angle of 22.8 °20 and the height of the minimum between peaks at 18 °20 which are characteristic of the crystalline and amorphous regions of cellulose, respectively. This method uses a ratio of the heights of the crystalline and amorphous regions to determine the crystallinity index, $\text{CrI} = \left( \frac{I_{002} - I_{AM}}{I_{002}} \right) \times 100$, where $I_{002}$ represents the crystalline peak height and $I_{AM}$ represents the measured amorphous region.\textsuperscript{27} Due to variation in peak widths, this method may overestimate the degree of crystallinity.\textsuperscript{28} However, due to its simplicity this method is widely used. The assignment of crystalline and amorphous regions is further illustrated in Figure 3.
Another method used for determining the degree of crystallinity from diffractograms is to separate crystalline and amorphous peaks by deconvolution. The crystallinity is then determined from the ratio of crystalline peak area to the total area of the diffractogram. A disadvantage of this method is the assumption that peak broadening is due to amorphous cellulose in the materials and not crystallite size or internal strain.27

Crystallite size can be determined using the measurement of the width of peaks at half of the maximum intensity as described by the Scherrer equation. This equation uses the relation $L = \frac{K\lambda}{\beta \cos \theta}$ where $L$ is the mean size of the crystalline domains, $K$ is the shape factor of the peak, which is usually taken as approximately 0.9, $\lambda$ is the x-ray wavelength used for the measurement, $\beta$ is the line broadening at half of the maximum
peak intensity (full-width half-maximum, FWHM) in radians and \( \theta \) is the Bragg angle which describes the scattering from a crystal lattice.\textsuperscript{29,30}

The crystallite size also affects the physical and chemical characteristics of cellulosic materials. The distance between adjacent planes in the cellulosic lattice, termed the d-spacing, is also useful for the comparison of solid samples.\textsuperscript{31}

The main experimental method used in this research was thermogravimetric analysis (TGA). The thermodynamic and kinetic stability of cellulosic materials processed using the aforementioned methods were compared and examined. The crystallinity and crystal quality of CNCs and CNFs and their starting materials were also examined using XRD.
CHAPTER 2
EXPERIMENTAL METHODS

2.1. Materials

Freeze-dried samples of cellulose nanocrystals (CNCs) produced via sulfuric acid hydrolysis and cellulose nanofibers (CNFs) produced via TEMPO processing were obtained from USDA Forest Products Laboratory (FPL), Madison, WI, and analyzed as received. The dissolving pulps used as starting materials for preparing CNCs and CNFs were also provided by FPL and analyzed as received. The dissolving pulp used to prepare CNCs was machine dried, pre-hydrolysis, kraft, rayon grade, wood pulp and that used to make CNFs was eucalyptus dry-lap cellulose fibers.

American process Inc. (API), Atlanta, GA, provided freeze-dried samples of cellulose nanocrystals and cellulose nanofibers produced by the AVAP® process. Freeze-dried lignin-coated CNFs and CNCs, as well as eucalyptus wood chips and eucalyptus pulps used in the AVAP® production of CNFs and CNCs were also provided by API.
2.2. Calcium, Sodium, and Sulfur analyses of CNCs, CNFs, L-CNCs and L-CNFs

An elemental analysis of materials conducted at FPL yielded the results shown in Table 2. Samples were digested and analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Table 2. Results of the Elemental Analysis of Materials

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Weight Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calcium</td>
</tr>
<tr>
<td>AVAP® CNCs</td>
<td>0.008</td>
</tr>
<tr>
<td>AVAP® L-CNCs</td>
<td>0.021</td>
</tr>
<tr>
<td>AVAP® CNFs</td>
<td>0.009</td>
</tr>
<tr>
<td>AVAP® L-CNFs</td>
<td>0.047</td>
</tr>
<tr>
<td>FPL CNCs</td>
<td>0.000</td>
</tr>
<tr>
<td>FPL TEMPO CNFs</td>
<td>0.000</td>
</tr>
</tbody>
</table>

2.3.1. Instrumentation - Thermogravimetric Analysis (TGA)

Thermal analyses of samples were conducted using a TA Instruments Thermogravimetric Analyzer (TGA) Q50. Samples (11 ± 2 mg) were placed into a platinum sample pan which was suspended freely from a hanging balance. The samples were then heated in the sample pan at multiple linear heating rates of 2, 5, 10, 15 and 20 °C/min under nitrogen from 30 °C to either 400 or 450 °C depending on observed thermal stability.
Kinetic parameters were calculated using Microsoft Excel as well as the TA Specialty Library software. The model-fitting and model-free methods, and the Arrhenius equation were used as described in Chapter 1.

2.3.2. Instrumentation - X-ray Diffraction (XRD) Analysis

XRD of materials was conducted using a PANalytical Empyrean diffractometer with a vertical goniometer in theta-theta geometry. The stage for flat samples was used and samples were placed on a silicon wafer for measurement via a single scan. The incident beam was generated at a voltage of 45 kV and a current of 40 mA. The radiation used was CuKα radiation which consisted of Kα1 (1.541 Å) and Kα2 (1.544 Å) components. The source slits were 12.0 mm and 0.4 mm and the detector slit was 5.0 mm. The goniometer radius used for both was 240.0 mm. A large beta nickel filter was used and the detector was a PIXcel3D 1x1 area detector. Scans were obtained from 10 to 50 degrees 2θ in 0.0657 degree steps for 30 seconds per step.

The data obtained from the diffractometer were used to calculate the degree of crystallinity as well as the crystallite size. The degree of crystallinity was calculated using the height ratio between the intensity of the crystalline peak (I002), observed at \( \sim 22.0 \, ^\circ 2\theta \), and the amorphous region (IAM) usually observed around 18.0 \( ^\circ 2\theta \) for cellulosic materials. The percentage representing the crystallinity index was given by the relation \( \left( \frac{I_{002} - IAM}{I_{002}} \right) \times 100 \).
CHAPTER 3
RESULTS AND DISCUSSION

3.1 Introduction

Nanocellulose has been produced by a variety of different methods, however, the influence of these processes on the nanocellulosic product has not yet been examined or compared using thermal analysis. Thermal analysis has been utilized on a very limited basis to analyze the thermal stability of nanocellulose.\textsuperscript{11,27} The International Organization for Standardization (ISO) has published draft standards on the nomenclature to be used for nanocellulose materials, as well as standards for techniques used in its analysis. This draft references the application of thermal analysis for the measurement of thermal stability of nanocellulose using thermogravimetric analysis (TGA); however, it was also suggested that previous studies had not directly compared TGA results for different methods of obtaining nanocellulose using identical thermogravimetric analytical parameters.\textsuperscript{11,27} Based on our interest in incorporating nanocellulose into polymer matrix composites it was important for us to determine its thermal properties.

For this study, both cellulose nanocrystals (CNCs) and cellulose nanofiber (CNFs) were obtained from the USDA FPL and API and examined by TGA and XRD using multiple methods and compared under identical conditions. CNFs and CNCs
produced via the AVAP® process as well as CNCs and CNFs produced via sulfuric acid hydrolysis (SAH) and the TEMPO process, respectively, were examined. Surface-modified versions of these materials termed L-CNCs and L-CNFs produced by the AVAP® process were also tested. The methods of preparation of these materials are described in Chapter 1.

3.2. Thermogravimetric Analysis

Thermogravimetric analysis was the core technique used in this study. TGA experiments were carried out at varying temperature ramp rates and the nanocellulose material response was recorded and analyzed. Figure 4 depicts a representative thermogram of weight loss versus temperature obtained for the eucalyptus dissolving pulp used to prepare the FPL CNCs at a ramp rate of 10 °C/min under N2. This figure shows how the onset of degradation was determined using the intersection of two tangents, one drawn from the start of major degradation and the other drawn along the curve during the degradation event. The initial weight loss, up to ~100 °C, was due to the evaporation of the surface water on the CNCs. Following this, very little mass is lost up to ~290 °C then rapid thermal degradation was observed. The percentage mass which remained after the major degradation event is referred to as the residual mass which is due to the inorganic components of the CNCs and CNFs. This figure also depicts the derivative (DTG) of percent weight loss with respect to temperature which was used to determine the temperature of maximum rate of weight loss, the peak of the derivative curve.
Figure 4. Thermogram showing the weight % vs. T and the derivative of percent weight loss with respect to temperature curves obtained for the eucalyptus dissolving pulp used for sulfuric acid hydrolysis CNCs at a ramp rate of 10 °C/min under N₂.

Figure 5 depicts representative thermograms of weight % versus temperature obtained for CNFs produced via the AVAP® and TEMPO processes as well as CNCs produced by the AVAP® and sulfuric acid hydrolysis processes at a ramp rate of 10 °C/min under N₂.
Figure 5. TGA curves showing weight loss vs. temperature for AVAP® CNCs and CNFs, and FPL produced CNCs, and TEMPO CNFs at 10° C/min under N₂.

API has surface-modified CNCs and CNFs by depositing lignin on to the surface of the fibrils or crystals. This leads to the production of nanocellulose derivatives with low hydrophobicity and increased compatibility with organic polymers. Figures 6 and 7 show thermograms obtained for samples heated at 10 °C/min under N₂. The onset of degradation temperatures was found to be higher for the lignin coated NCs than the corresponding untreated NCs.
Figure 6. TGA curves showing the comparison of L-CNCs and CNCs produced by the AVAP® process heated at 10 °C/min under N₂.
Figure 7. TGA curves showing the comparison of L-CNFs and CNFs produced by the AVAP® process heated at 10 °C/min under N₂.

3.3. Model-fitting and Model-free Methods

A variety of methods have been developed to analyze and fit TGA data. The earliest methods used to obtain kinetic parameters were model-fitting methods. Models of this kind were based on approximations of how the shape of individual particles changed as weight loss occurred. Mathematical models were then developed to predict kinetic parameters using these approximations as well as the extent of degradation (α),
where $\alpha = \frac{(m_0 - m_T)}{(m_0 - m_F)}$. In this equation, $m_0$ is the initial mass of the sample, $m_F$ is the final mass of the sample, and $m_T$ is the mass of the sample at a particular temperature in Kelvin. An integrated rate law model function, $g(\alpha) = kt$, where $k$ is the rate constant and $t$ is time, was developed to mathematically predict physical changes as the degradation progresses. Since $g(\alpha) = Ae^{(-E_a/RT)}$, the Arrhenius expression, where $A$ is the pre-exponential factor, $E_a$ is the activation energy, $R$ is the gas constant, and $T$ is the temperature in Kelvin, graphs of $\frac{g(\alpha)}{T^2}$ vs. $1/T$ should result in a straight line as the function is linear in cases where the data fit the models. If the data fit the models, kinetic parameters can be determined from the straight line plots. A graph of $ln \left[ \frac{g(\alpha)}{T^2} \right]$ vs. $1/T$ should give $A$ and $E_a$ from the intercept and slope, respectively. Varying ramp rates are used to obtain $\alpha$. Table 3 gives a summary of the twelve highly used mathematical functions, $g(\alpha)$, utilized in model-fitting methods to analyze solid state reactions by TGA. Models 1-6 are nucleation models, 7 and 8 are diffusion models, 9 and 10 are reaction order models and 11 and 12 are geometrical contraction models. These models are described in detail in Chapter 1.
Table 3. Solid state reaction models (mathematical functions) for model-fitting of weight loss vs. temperature of TGA data$^{22}$

<table>
<thead>
<tr>
<th>Model Number</th>
<th>Model Name</th>
<th>$g(\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Power Law</td>
<td>$\alpha^{1/4}$</td>
</tr>
<tr>
<td>2</td>
<td>Power Law</td>
<td>$\alpha^{1/3}$</td>
</tr>
<tr>
<td>3</td>
<td>Power Law</td>
<td>$\alpha^{1/2}$</td>
</tr>
<tr>
<td>4</td>
<td>Avrami-Erofeev</td>
<td>$[-\ln (1 - \alpha)]^{1/4}$</td>
</tr>
<tr>
<td>5</td>
<td>Avrami-Erofeev</td>
<td>$[-\ln (1 - \alpha)]^{2/3}$</td>
</tr>
<tr>
<td>6</td>
<td>Avrami-Erofeev</td>
<td>$[-\ln (1 - \alpha)]^{1/2}$</td>
</tr>
<tr>
<td>7</td>
<td>1-Dimensional diffusion</td>
<td>$\alpha^2$</td>
</tr>
<tr>
<td>8</td>
<td>Diffusion control (Janders)</td>
<td>$[1 - (1 - \alpha)^{1/3}]^2$</td>
</tr>
<tr>
<td>9</td>
<td>Mampel First Order</td>
<td>$-\ln(1 - \alpha)$</td>
</tr>
<tr>
<td>10</td>
<td>Mampel Second Order</td>
<td>$(1 - \alpha)^{-1} - 1$</td>
</tr>
<tr>
<td>11</td>
<td>Contracting cylinder</td>
<td>$1 - (1 - \alpha)^{1/2}$</td>
</tr>
<tr>
<td>12</td>
<td>Contracting sphere</td>
<td>$1 - (1 - \alpha)^{1/3}$</td>
</tr>
</tbody>
</table>

Figures 8, 9 and 10 are representative graphs showing the application of each of the solid state reaction models in Table 3 in order to obtain kinetic parameters from the slope and intercept from the desired straight line fit. It was clearly observed that the thermal degradation of the nanocellulosic materials did not fit these models, as straight lines were not obtained with any of these models.
Figure 8. Representative graphs showing the application of nucleation model-fitting methods, equations 1 – 6 as in Table 3, to data obtained from FPL CNCs.
Figure 9. Representative graphs showing the application of diffusion model-fitting methods, equations 7 and 8 in Table 3, to data obtained from FPL CNCs.
It is clear that our experimental data do not fit these model-fitting methods. Hence, model-free methods, which are also called isoconversional methods, were applied to the data in order to determine fit and calculate the kinetic parameters. Model-free methods are based purely on mathematical models that assume a chemical reaction that follows an Arrhenius relationship, whereas model-fitting methods are based on physical changes in the solid state as the mass of the material decreases as a function of temperature.
The primary model-free method used was the Snyder et al. modification of the Kissinger method. Kissinger proposed that the order and activation energy of reactions could be determined using the variation in the DTG peaks obtained from thermal analysis utilizing multiple ramp rates. As with model-fitting methods, straight lines should be obtained if the data fit the model from which kinetic parameters could be calculated. Kissinger developed this method to analyze pure samples and it was later modified by Snyder et al. for use with biological samples containing multiple components. The Snyder modification of the Kissinger methods has been utilized to obtain kinetic information on the thermal degradation of biopolymers, bacteria and small biochemical species.

Other mathematical models used were the modified Coats-Redfern, Friedman and Ozawa-Flynn-Wall methods. These methods are summarized in Table 1. For the Coats-Redfern method, the final equation developed to treat TGA data was

\[
\ln \left( \frac{\frac{\beta}{T^2 \left(1 - \frac{2RT}{E_a}\right)}}{\frac{-A_R}{E_a \ln(1-\alpha)}} \right) = -\frac{E_a}{RT} \cdot \frac{\ln \left( \frac{\beta}{T_m T} \right)}{T} \cdot \frac{1}{T}
\]

The data is analyzed by plotting \( \ln \left( \frac{\beta}{T_m T} \right) \) vs. \( \frac{1}{T} \) where \( \beta \) is the heating rate, \( T \) is the temperature, and \( T_m \) is the temperature of the maximum rate of weight loss, with \( T \) and \( T_m \) in Kelvin. In this case, the activation energy could be calculated using the relationship slope = \( -\frac{E_a}{R} \). This calculation can be carried out at varying degrees of conversion, \( \alpha \). The Friedman method uses the relationship:

\[
\ln \left( \frac{\frac{d\alpha}{dt}}{A \left(1 - \alpha\right)} \right) = \ln \left( \frac{\beta \left(\frac{d\alpha}{dt}\right)}{E_a} \right) = \ln A + \ln \left(1 - \alpha\right) - \frac{E_a}{RT} \cdot \frac{1}{T}
\]

The experimental data is analyzed by plotting \( \ln \left[\beta \left(\frac{d\alpha}{dt}\right)\right] \) vs. \( \frac{1}{T} \) where \( \beta \) represents the heating rate, \( \frac{d\alpha}{dt} \) represents the derivative peak obtained from the
percent weight loss with respect to temperature. This also gives rise to the activation energy using the relation slope = \left(\frac{-E_a}{R}\right). For the O-F-W method, the mathematical equation developed to model this data is; 
\[
\log(\beta) = A \log\left(\frac{4.5}{R} - \log(g(\alpha)) - 2.315 - 0.4567 \frac{E_a}{RT}\right).
\]
The data is analyzed by plotting \(\log(\beta)\) vs. \(\frac{1}{T}\). While the Friedman and Coats-Redfern methods are differentially obtained, the O-F-W method is based on an integral equation. As such, the relation is slope = \left(\frac{-0.4567}{R}\right). Representative graphs of each method for multiple degrees of conversion are shown below. Figure 11 represents the application of the Coats-Redfern model-free method to API CNCs. Each trend line represents a degree of conversion and comprises 5 data points, one each from the 2, 5, 10, 15 and 20 °C/min heating rates. The trend lines for the degrees of conversion increase in conversion percentage from 6% to 90% from right to left. Figures 12 and 13 give representative plots of the application of the O-F-W and Friedman model-free methods to AVAP® CNCs.
Figure 11. Representative graph showing the application of the Coats-Redfern method to AVAP® CNCs. The degree of conversion increases from right to left and is represented by the respective trend lines.
Figure 12. Representative graph showing the application of the O-F-W method to AVAP® CNCs. The degree of conversion increases from right to left and is represented by the respective trend lines.
Figure 13. Representative graph showing the application of the Friedman method to AVAP® CNCs. The degree of conversion increases from right to left and is represented by the respective trend lines.

The activation energies for the thermal decomposition of CNCs were obtained from these plots. The energies obtained were used to create plots of degree of conversion (α) vs. activation energy for the samples tested. This is shown in Figure 14.
Figure 14. Representative graphs showing the activation energies calculated using the Coats-Redfern method vs. the degree of conversion, $\alpha$, for AVAP® CNCs, CNFs, L-CNCs, L-CNFs and FPL CNCs and CNFs.

It can be seen from Figure 14 that the activation energies for the thermal degradation of the AVAP® CNCs, CNFs, L-CNCs, L-CNF remained relatively stable as a function of degree of conversion, $\alpha$, suggesting a high degree of homogeneity of these materials. On the other hand, the activation energies for the thermal degradation of the sulfuric acid hydrolysis and TEMPO CNCs and CNFs, respectively, varied dramatically as a function of $\alpha$, suggesting that these materials were less homogeneous. Based on the
onset of thermal degradation measured for CNCs and CNFs, the relative order of activation energies in Figure 14 are counter intuitive.

Utilizing the Snyder modification of the Kissinger method, we could determine both the activation energy $E_a$ and the pre-exponential factor, $A$. The DTG curves obtained using temperature programs of 2, 5, 10, 15 and 20 °C/min under nitrogen gave 5 maxima which vary as a function of temperature as shown in Figure 15. Figure 16 shows that representative experimental data fits the Kissinger model and that a plot of $\ln \left( \frac{\beta}{T_m^2} \right)$ vs. $\frac{1}{T}$ gave a straight line which showed good fit with the differential mathematical equation

$$\frac{d\left[\ln \left( \frac{\beta}{T_m^2} \right) \right]}{d\left( \frac{1}{T_m} \right)} = -\frac{E_a}{R}.$$ 

Since the data accurately fit this model as indicated by the high value for the coefficient of correlation ($R^2 = 0.9981$), the straight lines obtained for each sample were used to calculate kinetic parameters. The graphs for all samples are given in Appendix A. Error bars were excluded because they were smaller than the data point symbols.
Figure 15. Representative DTG curves for the dissolving pulp used to prepare CNCs by sulfuric acid hydrolysis. Curves A, B, C, D and E represent the ramp rates of 2, 5, 10 15 and 20 °C/min, respectively, under N$_2$. 
3.4. Calculation of Kinetic Parameters

Table 4 lists the onset of decomposition temperature (ramp rate of 10 °C/min), the corresponding DTG peak, residual mass, activation energy ($E_a$), the pre-exponential factor ($A$), and the calculated half-life at 165 °C (438 K) for the API CNCs, CNFs, L-CNCs and L-CNFS and eucalyptus chips from which they were obtained by the AVAP process. The half-lives were calculated at 438 K as this is the temperature used by our research group for processing these materials into polymer matrix composites. CNCs and CNFs are prepared by the AVAP process; however, a longer treatment time is used to prepare CNCs than is used to prepare CNFs. The eucalyptus chips which are composed...
of multiple components give rise to two DTG peaks which were treated independently utilizing the Snyder modification of the Kissinger method, the corresponding two sets of measured and calculated data are also included in Table 4. The data in Table 4 indicate that the AVAP nanocellulose extraction process does not appreciably reduce the thermal stability of the nanocellulose relative to the cellulose in the starting material.

Table 4. Kinetic Parameters calculated for AVAP® Samples using the Kissinger Method modified by Snyder et al.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$T_d$, ramp rate of 10 °C/min</th>
<th>Residual Mass (%)</th>
<th>DTG Peak Max, 10 °C/min</th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$ (s⁻¹)</th>
<th>$t_{1/2}$ at 165 °C (438 K) (s) (min in parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVAP® CNC</td>
<td>334 °C (607 K)</td>
<td>7.00</td>
<td>363 °C (636 K)</td>
<td>131</td>
<td>3.11x10⁸</td>
<td>8.66x10⁶ (1.44x10⁵ min)</td>
</tr>
<tr>
<td>AVAP® CNF</td>
<td>313 °C (586 K)</td>
<td>10.8</td>
<td>351 °C (624 K)</td>
<td>144</td>
<td>7.17x10⁹</td>
<td>1.24x10⁷ (2.07x10⁵ min)</td>
</tr>
<tr>
<td>AVAP® L-CNC</td>
<td>332 °C (605 K)</td>
<td>6.31</td>
<td>360 °C (633 K)</td>
<td>148</td>
<td>1.23x10¹⁰</td>
<td>2.85x10⁷ (4.75x10⁵ min)</td>
</tr>
<tr>
<td>AVAP® L-CNF</td>
<td>339 °C (612 K)</td>
<td>5.98</td>
<td>368 °C (641 K)</td>
<td>142</td>
<td>2.58x10⁹</td>
<td>2.29x10⁷ (3.82x10⁵ min)</td>
</tr>
<tr>
<td>Eucalyptus Chips</td>
<td>324 °C (598 K)</td>
<td>17.1</td>
<td>288 °C (561 K)</td>
<td>144</td>
<td>2.30x10¹¹</td>
<td>4.48x10⁵ (7.47x10³ min)</td>
</tr>
</tbody>
</table>

$T_d$ is the onset of degradation temperature, $E_a$ is the activation energy, $A$ is the pre-exponential factor, and $t_{1/2}$ is the half-life.
The kinetic parameters which were calculated for the CNCs made via sulfuric acid hydrolysis are shown in Table 5. These were obtained by hydrolyzing the amorphous regions of the cellulose using 64% sulfuric acid. It has been found that a concentration range of 60 – 64% is ideal as the amorphous regions may be removed without damage to the crystalline regions. This step was followed by dilution and filtration to obtain the CNCs. This table also includes the kinetic parameters calculated for the dissolving pulp which was used as the source material for the CNCs. The data in Table 5 clearly indicate that the sulfuric acid hydrolysis of cellulose leads to nanocellulose (CNCs) that have a much lower thermal stability than the cellulose from which they were prepared.

Table 5. Kinetic parameters calculated for CNCs produced by sulfuric acid hydrolysis and corresponding source material using the Snyder modification of the Kissinger model

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$T_d$, ramp rate of 10 °C/min</th>
<th>Residual Mass (%)</th>
<th>DTG Peak Max, 10 °C/min</th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$ (s$^{-1}$)</th>
<th>$t_{1/2}$ at 165 °C (438 K) (s) (min in parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNCs produced by SAH</td>
<td>287 °C (560 K)</td>
<td>26.7</td>
<td>302 °C (575 K)</td>
<td>175</td>
<td>7.53x10$^{13}$</td>
<td>5.89x10$^6$ (9.82x10$^4$ min)</td>
</tr>
<tr>
<td>Dissolving Pulp used for SAH CNCs</td>
<td>338 °C (611 K)</td>
<td>13.0</td>
<td>365 °C (638 K)</td>
<td>166</td>
<td>3.13x10$^{11}$</td>
<td>1.39x10$^8$ (2.32x10$^6$ min)</td>
</tr>
</tbody>
</table>

$T_d$ is the onset of degradation temperature, $E_a$ is the activation energy, $A$ is the pre-exponential factor, and $t_{1/2}$ is the half-life.
Table 6 gives the onset of decomposition temperature (ramp rate of 10° C/min),
the corresponding DTG peak, residual mass, activation energy $E_a$, pre-exponential
factory ($A$), and the calculated half-life at 165 °C for the CNFs prepared by the TEMPO
process and the corresponding dissolving pulp from which they were prepared. The data
in Table 6 clearly indicate that the TEMPO oxidation of cellulose leads to CNFs that
have a much lower thermal stability than the cellulose from which they were prepared
and less thermally stable than CNCs prepared by sulfuric acid hydrolysis.

Table 6. Kinetic parameters calculated for CNFs produced by the TEMPO process and
the corresponding starting material using the Snyder modification of the Kissinger model

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$T_d$, ramp rate of 10 °C/min</th>
<th>Residual Mass (%)</th>
<th>DTG Peak Max, 10 °C/min</th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$ (s$^{-1}$)</th>
<th>$t_{1/2}$ at 165 °C (438 K) (s) (min in parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPL TEMPO CNFs (0.65 mmol/g Na)</td>
<td>233 °C (506 K)</td>
<td>26.5</td>
<td>249 °C (521 K)</td>
<td>124</td>
<td>2.55x10$^{10}$</td>
<td>1.59x10$^{4}$ (2.64x10$^{2}$ min)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300 °C (572.77 K)</td>
<td>155</td>
<td>1.37x10$^{12}$</td>
<td>1.69x10$^{6}$ (2.81x10$^{4}$ min)</td>
</tr>
<tr>
<td>FPL TEMPO CNFs (1.3 mmol/g Na)</td>
<td>215 °C (488 K)</td>
<td>30.4</td>
<td>232 °C (202 K)</td>
<td>174</td>
<td>1.29x10$^{16}$</td>
<td>3.39x10$^{4}$ (5.66x10$^{2}$ min)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>281 °C (554 K)</td>
<td>193</td>
<td>1.79x10$^{16}$</td>
<td>3.88x10$^{6}$ (6.46x10$^{4}$ min)</td>
</tr>
<tr>
<td>Dissolving pulp - FPL TEMPO CNFs</td>
<td>332 °C (605 K)</td>
<td>13.7</td>
<td>362 °C (635 K)</td>
<td>152</td>
<td>2.86x10$^{11}$</td>
<td>2.87x10$^{6}$ (4.78x10$^{4}$ min)</td>
</tr>
</tbody>
</table>

$T_d$ is the onset of degradation temperature, $E_a$ is the activation energy, $A$ is the pre-
exponential factor, and $t_{1/2}$ is the half-life.
3.5. Projection of Half-life vs. Temperature

We have determined the activation and pre-exponential factor for the thermal decomposition of nanocellulosic materials; however, it is difficult to evaluate this combination of numbers directly. Thus, we have combined these values using the Arrhenius equation, \( k = A e^{-E_a/RT} \), to predict the rate constant for the thermal decomposition as a function of temperature. Half-lives were calculated using the relation \( \frac{\ln(2)}{k} \), based on the assumption of first order thermal decomposition reactions.

Figure 17 shows a comparison of the projected half-lives of API CNCs produced via the AVAP® process and FPL CNCs produced via the sulfuric acid hydrolysis process. It can be seen that at temperatures below 150 °C, the rate of thermal decomposition is insignificant and the activation energy dominates the Arrhenius equation, the FPL CNCs are projected to be more stable than the corresponding AVAP® material. However, above this temperature, where the pre-exponential factor dominates the Arrhenius equation, the API CNCs have a lower rate of thermal decomposition than the corresponding FPL CNCs. Similar results are shown for the API vs. FPL CNFs in Figure 18; however, the crossover point is lower, at \( \sim 125 \) °C.
Figure 17. Comparison of projected half-lives for API and FPL CNCs as a function of temperature.
Figure 18. Comparison of projected half-lives for API and FPL CNFs as a function of temperature.

A comparison of half-lives vs. temperature was also projected for the two batches of FPL CNFs, 0.65 mmol/g Na and 1.3 mmol/g Na, to determine if the difference in composition made a significant difference in the stability of the final nanocellulosic product. This is shown in Figure 19.
3.6. Calcium, Sodium, and Sulfur analyses of CNCs, CNFs, L-CNCs and L-CNFs

CNCs and CNFs were analyzed for calcium, sodium, and sulfur by ICPAES at FPL to further characterize the nanomaterials studied in this project and the results are
summarized in Chapter 2 and in Figure 20. Sulfur and sodium content in the FPL CNCs reflects the fact that the surface of the CNCs have been sulfonated during the sulfuric acid hydrolysis process. The high sodium content in the FPL TEMPO CNFs reflects the degree of oxidation of the C₆ OH group. The low Na and S content of the materials prepared by the AVAP® process reflects that this process only minimally modifies that surface of the CNCs and CNFs produced by this method.

Figure 20. Graph showing the Ca, Na, and S content of the CNCs, CNFs, L-CNCs and L-CNFs investigated.
3.7. X-ray Diffraction Analysis of CNCs and CNFs

CNCs and CNFs were characterized by using X-ray diffraction (XRD). Figure 21 gives an example of a diffractogram obtained. Figure 22 shows how the diffractogram in Figure 21 analyzed using the PANalytical HighScore software package, including peak deconvolution and peak selection. The valley at approximately 18°2θ is representative of the amorphous region (IAM) and the peak at approximately 22.5°2θ is representative of the crystalline region (I002) of the cellulosic samples. The differences in height between the projected background and the deconvoluted peaks at these positions were used to calculate the degree of crystallinity for the samples are given in Table 7 by CrI =

\[
\left( \frac{I_{002} - I_{AM}}{I_{002}} \right) \times 100.
\]

Figure 21. XRD diffractogram obtained for the dissolving pulp used to prepare CNCs by sulfuric acid hydrolysis.
Figure 22. XRD diffractogram obtained for the FPL dissolving pulp used in the production of CNCs and adjusted by HighScore.
Table 7. Degrees of Crystallinity calculated for the nanocellulosic materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degree of Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPL CNFs*</td>
<td>80.00</td>
</tr>
<tr>
<td>FPL CNCs</td>
<td>89.47</td>
</tr>
<tr>
<td>FPL Dissolving pulp used for CNFs</td>
<td>89.58</td>
</tr>
<tr>
<td>FPL Dissolving pulp used for CNCs</td>
<td>87.80</td>
</tr>
<tr>
<td>API CNFs</td>
<td>84.38</td>
</tr>
<tr>
<td>API CNCs</td>
<td>87.88</td>
</tr>
<tr>
<td>API Eucalyptus pulp for CNFs</td>
<td>92.45</td>
</tr>
<tr>
<td>API Eucalyptus pulp for CNCs</td>
<td>92.43</td>
</tr>
</tbody>
</table>

* FPL CNF containing 1.3 mmol Na.

These results suggested that there is little difference between the final FPL CNCs and CNFs and the API CNCs and CNFs, with respect to degree of crystallinity. The Scherrer equation, as described in Chapter 1, was then used to calculate crystallite size of the CNCs and CNFs assuming no internal strain. The results of these calculations are shown in Table 8. The primary crystalline peak (22.5 ° 2θ) was used for these calculations.
Table 8. Crystallite sizes of nanocellulosic materials as calculated using the Scherrer Method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystalline Peak</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position [°2θ]</td>
<td>d-spacing [Å]</td>
</tr>
<tr>
<td>FPL CNC</td>
<td>22.79</td>
<td>3.90</td>
</tr>
<tr>
<td>FPL CNF**</td>
<td>22.93</td>
<td>3.88</td>
</tr>
<tr>
<td>Dissolving Pulp for CNCs</td>
<td>23.03</td>
<td>3.86</td>
</tr>
<tr>
<td>Dissolving Pulp for CNFs</td>
<td>23.01</td>
<td>3.86</td>
</tr>
<tr>
<td>API CNC</td>
<td>22.62</td>
<td>3.93</td>
</tr>
<tr>
<td>API CNF</td>
<td>23.07</td>
<td>3.85</td>
</tr>
<tr>
<td>API Eucalyptus Pulp for CNCs</td>
<td>23.05</td>
<td>3.85</td>
</tr>
<tr>
<td>API Eucalyptus Pulp for CNFs</td>
<td>23.14</td>
<td>3.81</td>
</tr>
</tbody>
</table>

*FWHM refers to the full width of the peak at half of its maximum.
**FPL CNF containing 1.3 mmol Na.
CONCLUSION

We have examined and compared the thermal stability of CNCs and CNFs prepared by the sulfuric acid hydrolysis, TEMPO, and AVAP® processes and the corresponding starting materials by thermogravimetric analysis (TGA). TGA data allowed the determination of the onset of decomposition temperature, activation energy ($E_a$) and pre-exponential factor ($A$) for the thermal degradation of these materials under nitrogen. It was found that the AVAP® nanocellulose extraction process does not appreciably reduce the thermal stability of the nanocellulose relative to the cellulose in the starting material. Sulfuric acid hydrolysis of cellulose gives CNCs that have a much lower thermal stability than the cellulose from which they were prepared. The TEMPO oxidation of cellulose leads to CNFs that have much lower thermal stability than the cellulose from which they were prepared and less thermally stability than CNCs prepared by sulfuric acid hydrolysis. The lower pre-exponential factor determined for the AVAP® CNCs and CNFs relative to that for the FPL CNCs and CNFs prepared by sulfuric acid and TEMPO processes, respectively, more than compensates for the lower activation energy of decomposition, leading to higher thermal stability of AVAP® CNCs and CNFs at temperatures that are relevant to polymer and composite processing.

X-Ray Diffraction (XRD) was used to examine the degree of crystallinity and crystallite size of the CNCs, CNFs and the corresponding starting materials from which
they were prepared. The degree of crystallinity determined by XRD showed no
correlation with the thermal stability of the nanocellulose materials studied. However, it
was found that higher modification of the surface of CNCs and CNFs as evidenced by
Na, Ca, and S analysis correlated with the lower thermal stability of CNCs produced by
sulfuric acid hydrolysis and CNFs produced by TEMPO oxidation.
APPENDIX A

Graphs showing the application of Kissinger model-free methods to nanocellulosic materials

Graph showing the application of the Kissinger method to AVAP® CNCs.

\[ y = -15722x + 13.985 \]

\[ R^2 = 0.9826 \]
Graph showing the application of the Kissinger method to AVAP® CNFs.

\[ y = -17254x + 17.032 \]

\[ R^2 = 0.9975 \]
Graph showing the application of the Kissinger method to AVAP® L-CNCs.
Graph showing the application of the Kissinger method to AVAp® L-CNFs.

\[ y = -17077x + 16.021 \]

\[ R^2 = 0.9938 \]
Graph showing the application of the Kissinger method to FPL TEMPO CNFs (1.3 mmol/g Na).
Graph showing the application of the Kissinger method to FPL TEMPO CNFs (0.65 mmol/g Na).
Graph showing the application of the Kissinger method to FPL CNCs.
Graph showing the application of the Kissinger method to the dissolving pulps used to produce FPL TEMPO CNFs.
APPENDIX B

Representative graphs showing reproducibility tests
REFERENCES


