

New York State Energy Research and Development Authority

Evaluation of Microwave Pretreatment for Reducing the Recalcitrance of Woody Biomass to Hemicellulose Extraction and Cellulose Hydrolysis

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**EVALUATION OF MICROWAVE PRETREATMENT FOR
REDUCING THE RECALCITRANCE OF WOODY BIOMASS TO
HEMICELLULOSE EXTRACTION AND CELLULOSE HYDROLYSIS**

Final Report

Prepared for the
**NEW YORK STATE
ENERGY RESEARCH AND
DEVELOPMENT AUTHORITY**



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ABSTRACT

The extreme recalcitrance of lignocellulosic substrates to hydrolysis requires substrate pre-treatment to facilitate the conversion of woody biomass to renewable fuels and bioproducts. Unfortunately, these pre-treatments are energy intensive and costly, involving the use of intense physical and thermo chemical pretreatments. Unless this problem is satisfactorily resolved, it is unlikely that the promise of lignocellulosic feedstock use for biofuel production will be fully realized. This research examined the use of microwave energy as a tool to reduce the recalcitrance of both hemicellulose and cellulose within the biomass matrix. The investigation involved exposure of willow, pine and maple wood feedstocks to microwave radiation at atmospheric pressure and pressurized conditions, with and without selected amendments, with power levels ranging from 1 kW to 40 kW. The research focused on feedstock exposure at atmospheric conditions. The goal was to establish whether increased power levels could induce superheated conditions in the wood structure capable of breaking down the woody matrix. The results showed that such breakdown tends to be primarily macroscopic and does not sufficiently disrupt the cellular wood structure necessary to enhance hemicellulose extraction or enzymatic hydrolysis beyond that which would be expected by conventional heating processes. Pressurized high temperature superheated conditions were found to be necessary to induce the desired breakdown of the biomass.

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SUMMARY

BACKGROUND

The extreme recalcitrance of lignocellulosic substrates to hydrolysis requires substrate pre-treatment to facilitate the conversion of woody biomass to renewable fuels and bioproducts. Unfortunately, these pre-treatments are energy intensive and costly, involving the use of intense physical and thermo chemical pretreatments.

The most common chemical pretreatment methods used for cellulosic feedstocks make use, after milling, of high temperature and pressure reactors employing dilute acid, alkaline, organic solvent, ammonia, sulfur dioxide, carbon dioxide or other chemicals to make the biomass more digestible by the enzymes. Biological pretreatments are sometimes used in combination with chemical treatments to depolymerize and solubilize the lignin in order to make cellulose more accessible to hydrolysis and fermentation.

Each type of feedstock, whether softwoods, corn stover or bagasse, requires a particular combination of pretreatment methods to optimize the yields of that feedstock, minimize the degradation of the substrate, and maximize the sugar yield. Pretreatment of cellulosic biomass in a cost-effective manner is a major challenge of cellulose-ethanol technology research and development and is arguably the limiting step to effective lignocellulosic use as a biofuel feedstock. Unless this problem is satisfactorily resolved, it is unlikely that the promise of lignocellulosic feedstock use for biofuel production will be fully realized.

OBJECTIVES

The research effort and the results described in this report were designed to determine if microwave radiation, properly employed, could reduce lignocellulosic recalcitrance by inducing, through direct or indirect reactions, transformations in the woody structure of the material. Mechanistically, the goal was to determine whether microwave radiation could alter the lignocellulosic matrix in such a way so as to provide improved access of reagents and enzymes to the functional components of the matrix (hemicellulose, lignin and cellulose), over and beyond non-microwave approaches.

From a practical standpoint, employing microwave energy in high- pressure reactors would entail the development of new microwave application systems that presently do not exist. It was projected that the costs and operation of such systems would be prohibitive. As a result, the research undertaken focused on the application of microwave energy under atmospheric (not pressurized) conditions. It was projected that if recalcitrance reduction due to the microwave radiation could be shown, then operating at atmospheric conditions could dramatically reduce capital and operating costs associated with biomass pretreatment systems, providing improved potential for developing a cost effective commercially viable system.

RESEARCH APPROACH

The research approach undertaken focused on the treatment of willow, pine and maple chips using microwave radiation from low power (1 kW), medium power (3.2 kW) and high power (15 to 40 kW) microwave applicators.

The general analytical strategy involved in the evaluation included:

- The preparation of selected feedstock samples (willow and pine in small log shapes and maple wood in chip form) for testing
 - For maple wood samples, the moisture content was adjusted prior to microwave treatment, providing saturated and supersaturated samples for testing; and amendments were added (acetic acid and/or sodium chloride) to the supersaturated (excess) liquid in the chip-liquor solution
 - Willow and pine samples were processed as received (green).
- Exposure of the feedstock samples to microwave energy in one or more of the available applicators for selected durations
- The conduct of extraction tests after microwave pretreatment to quantify solids and/or hemicellulose extraction, or glucose production (enzymatic hydrolysis) of the pretreated samples. The results were compared to control samples that were comprised of hot water treated samples or untreated samples to assess the relative microwave effects.

The primary objective of the **low power tests** was to determine if the exposure of a lignocellulosic feedstock (maple wood chips) to low power microwave radiation in pressurized and unpressurized vessels, and with or without selected amendments could degrade the feedstock sufficiently to enhance the extraction of hemicellulose from the feedstock above levels achievable using conventional hot water extraction methods. To undertake this effort, a series of specially designed tests were designed using maple wood chips and low power microwave applicator equipment. Tests were conducted in both pressurized vessels where superheated steam could be generated, and in non-pressurized vessels where steam was vented to the atmosphere. The maple wood chips were moisture conditioned prior to microwave exposure, and also amended with acetic acid (HAc) and sodium chloride (NaCl).

The primary objective of **the medium power tests** was to determine if medium power application at atmospheric pressure conditions could be used to open the structure of woody biomass samples and enhance the extraction of hemicellulose (reduce sample recalcitrance), compared to conventional alkali extraction; and also affect the overall mechanical properties (measured as compressive strength) of the treated wood samples. The examination was designed to investigate whether steam explosions within the wood structure, induced by rapid internal heating by microwaves, could open the pore structure of the biomass and either enhance hemicellulose extraction and/or reduce wood strength. The goal of the wood strength reduction evaluation was to determine whether energy consumption associated with biomass milling might be reduced with lower strength biomass produced by microwave

pretreatment.¹ To achieve the aforementioned objectives willow stems were processed in a 3.2 kW commercial microwave oven. Processed samples were subjected to extraction and tested for hemicellulose content as well as compressive strength before and after microwave treatment.

High power testing included an examination of the effects of high power density exposure of willow, pine, and maple wood to microwave. The primary objective of the high power tests was to determine if an increase in microwave power density could induce a more dramatic breakdown in the recalcitrance of woody biomass to hemicellulose extraction and enzymatic hydrolysis than was suggested by the low and medium power test results. The basis for these tests was the premise that a high-applied power density could promote a very rapid generation of internal superheated steam in the source material with mini internal “steam explosions” in the porous and cellular structure of the feedstock. It was also assumed that if the internal pressure could not be rapidly dissipated, due to a low surface area to volume ratio (A/V) of the wood sample, then the steam pressure buildup inside the matrix would be more likely to induce micro-(cellular) structural transformations, when compared to a sample with a high A/V ratio. The test program was designed to examine these issues.

FINDINGS

The following is an outline summary of the findings of the **low power** testing effort:

- Under atmospheric pressure conditions where feedstock temperatures of only +/- 100°C could be achieved, maple chip mass breakdown was not significant
- Where temperatures above 140°C could be achieved, in pressurized reactors, maple chip mass breakdown in low solids conditions was measurable
- Amendment addition of acetic acid was found to be effective in improving woody mass breakdown, but only at elevated pressures and corresponding temperatures
- High solids processing (moisture contents between 7 and 50%) did not provide any measurable benefit over low solids (80% moisture content) in pressurized reactors
- In non-pressurized reactors the high solids samples dried rapidly and charred, if moisture was not maintained in the sample feedstock
- Observed microwave benefits could only be attributed to temperature effects. No special radiation effects were observed.

¹ Biomass preprocessing normally includes a milling step. Milling is an effective but costly way to increase the extraction of hemicellulose from lignocellulosic biomass. It is well known that mechanical pulping of wood at higher temperatures leads to a reduced consumption of pulping energy due to a softening of the wood.

The following is an outline summary of the findings of the **medium power** testing effort:

- Medium power microwave application (3.2 kW) applied under atmospheric conditions did not affect the woody feedstock structure or enhance extraction sufficiently to be used as a substitute for more aggressive alkali extraction methods
- Medium power microwave treatment did generate sufficient internal steam pressures to disrupt the macro-scale structure of the treated wood, however such breakdown did not affect the internal cellular structure of the wood matrix sufficiently to reduce recalcitrance above that which might be anticipated by any other hot water treatment
- Excessive microwave exposure will dry the biomass, resulting in an increase in wood strength and not the desired decrease.

The following is an outline summary of the findings of the **high power** testing effort:

- High power microwave application at atmospheric pressure generated moderate superheated temperatures within the woody sticks (willow and pine) tested
- A rapid release of moisture and drying of the wood was associated with all high power microwave tests
- High power microwave treatment did generate sufficient internal steam pressures in the willow and pine feedstocks to disrupt the macro-scale structure of the treated wood
- Glucose production (enzymatic hydrolysis) was reduced in willow and pine biomass, subjected to high power microwave application, and this was attributed to the drying of the wood and possibly the collapse of the pore structure of the biomass.

CONCLUSIONS

It was concluded from the investigation that:

- Microwave processing of biomass offers no special advantage over conventional heat processing
- To achieve measurable benefits, solution temperatures must approach 200°C, requiring the use of pressurized reactors
- The maintenance of adequate moisture in biomass feedstock or processing in a solution are the only practical ways to employ microwave in biomass pretreatment
- While high- powered microwave radiation can induce steam explosions inside the biomass structure and disrupt the macro-scale structure of the biomass, such explosions accompanied by the rapid loss of moisture and wood drying tends to increase the recalcitrance of the biomass, thereby reducing enzymatic hydrolysis yields.

RECOMMENDATIONS

It is recommended that future work on microwave will focus on their potential use in high- pressure microwave applicators, and the development of systems where sufficient moisture can be maintained during processing. A rapid increase in temperature without drying of the biomass could potentially induce macro-structural changes, due to internal steam explosions, and rapid buildup of superheated temperature conditions could induce micro-cellular changes that might enhance hemicellulose extraction and enzymatic hydrolysis.

Though this strategy increases the complexity of the application system, pressure and temperature conditions at atmospheric pressure were found to be insufficient to induce measurable biomass breakdown.

INTRODUCTION

This report presents a description of the activities and results of a study undertaken by a research team consisting of Thermex-Thermatron, Inc., headquartered in Louisville, KY, Chesner Engineering, P.C. of Long Beach, NY, and the College of Environmental Science and Forestry at the State University of New York in Syracuse. The purpose of the investigation was to evaluate the potential use of microwave energy to assist in the extraction of hemicellulose, and the hydrolysis of cellulose from woody biomass feedstocks.

The report is divided into several sections (see Table of Contents). These sections provide descriptions of the background and objectives of the investigation, relevant literature pertaining to the use of microwaves in the processing of lignocellulosic biofuel feedstocks, an experimental overview of the effort and detailed presentations of the testing program and the results of the study.

The results are presented in several sections that reflect the applied microwave power levels employed during the investigation. These sections and the referenced power levels are referred to as low power, medium power, and high power sections. While each section was designed as a stand-alone section, it is of note that the data generated during one stage of the study influenced decisions to conduct subsequent tests. For example, the initial testing program envisioned low and medium power testing, but during the course of the effort high power testing was introduced.

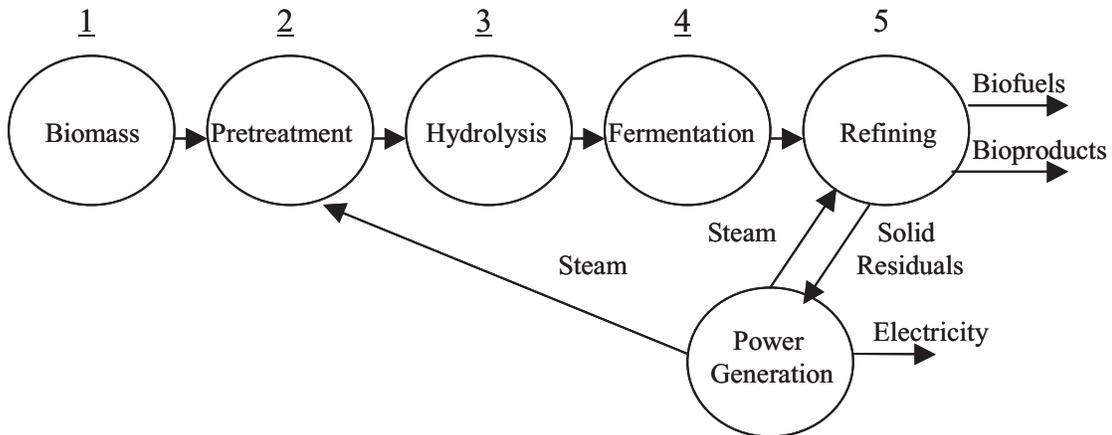
The final section of the report contains a summary of the findings, conclusions, and recommendations of the research team involved in the effort.

BACKGROUND AND OBJECTIVES

BACKGROUND

The conventional model for the development of a cellulosic ethanol biorefinery includes five key processing steps, listed below and depicted in the following sketch:

1. Cellulosic biomass from trees, grasses, or agricultural wastes harvested and delivered to the biorefinery,
2. Biomass ground into small, uniform particles and thermo chemical pretreatment to separate cellulose, from other biomass materials and open up the cellulose surface to enzymatic attack,
3. A mix of enzymes added to break down cellulose into simple sugars,
4. Microbes are introduced to produce ethanol by fermenting sugars from cellulose and other biomass carbohydrates,
5. Ethanol separated from water and other components of the fermentation broth and purified through distillation.



It is generally acknowledged that to reduce overall lignocellulosic-biomass to biofuel processing costs to practical levels, continued progress in the development of more cost effective pretreatment methods (Step 2) is needed. This step has been identified as the unit operation that is the second highest (after the feedstock harvesting cost component) in the entire process (Keller 2003). It is reported that mechanical pretreatment (milling) of lignocellulosic feedstocks into fine millimeter size particles alone can consume up to one-third of the energy used in the conversion process (Wooley 1999).

The pretreatment step (Step 2) involves a reduction in biomass size and the depolymerization, solubilization and separation of one or more of the four major components of biomass: hemicellulose, cellulose, lignin, and extractives, to make the remaining solid biomass more accessible to further chemical or biological treatment. There are numerous pretreatment methods or combinations of pretreatment methods available. The physical pretreatment

commonly used by the corn-ethanol producers is milling, which reduces the size of the corn kernel, opening it up for enzymatic hydrolysis.

Methods used for cellulosic materials, however, require much more intense physical and thermo chemical pretreatments (Chandra 2007). The most common chemical pretreatment methods used for cellulosic feedstocks make use, after milling, of high temperature and pressure reactors employing dilute acid, alkaline, organic solvent, ammonia, sulfur dioxide, carbon dioxide, or other chemicals to make the biomass more digestible by the enzymes. Biological pretreatments are sometimes used in combination with chemical treatments to depolymerize and solubilize the lignin in order to make cellulose more accessible to hydrolysis and fermentation. Each type of feedstock, whether softwoods, corn stover or bagasse, requires a particular combination of pretreatment methods to optimize the yields of that feedstock, minimize the degradation of the substrate, and maximize the sugar yield. Pretreatment of cellulosic biomass in a cost-effective manner is a major challenge of cellulose-ethanol technology research and development.

OBJECTIVES

The primary objective of the research effort undertaken was to determine if microwave radiation, properly employed could reduce lignocellulosic recalcitrance by inducing, through direct or indirect reactions, transformations in the woody structure of the material. Mechanistically, the goal was to determine whether microwave radiation could alter the lignocellulosic matrix in such a way so as to provide improved access of reagents and enzymes to the functional components of the matrix (hemicellulose, lignin and cellulose), over and beyond non-microwave approaches.

Prior researchers have shown that the exposure of ground biomass (e.g., wood chips) to microwave energy can rapidly generate superheated conditions (temperature and pressure) to reduce the recalcitrance of lignocellulosic substrates. Much of the prior work, however, has focused on the use of microwave radiation as an alternative energy source (to conventional steam heating or convection heat transfer) to elevate feedstock-processing temperatures. Most of the reported work was undertaken in superheated temperature environments.

From a practical standpoint, however, employing microwave energy in high- pressure reactors would entail the development of new microwave application systems that presently do not exist. It was projected that the costs and operation of such systems would be prohibitive. As a result, the research undertaken focused on the application of microwave energy under atmospheric (not pressurized) conditions. It was projected that operating at atmospheric conditions could dramatically reduce capital and operating costs associated with biomass pretreatment systems, providing improved potential for developing a cost effective commercially viable system.

RELEVANT MICROWAVE APPLICATION LITERATURE

PRE-2000 LIGNOCELLULOSIC PRETREATMENT LITERATURE

Since the early 1980s, researchers have studied and reported on a range of applications using microwave radiation for lignocellulosic feedstock processing.

Japanese Research (1980s)

Some of the earliest works on microwave induced enhanced enzymatic susceptibility were reported by Japanese researchers. Azuma reported that rice straw (Azuma, 1984) and softwoods (Azuma 1985) could be made enzymatically susceptible when these materials were pretreated under pressure (sealed containers) in a 2.3 kW microwave oven reactor at a temperature of 230 deg. C for 5-7 minutes. Ooshima similarly reported successful results irradiating rice straw and bagasse with microwave in sealed glass vessels, at temperatures of 170–200 deg C for five minutes (Ooshima, 1984). Magara reported on the use microwave radiation for the pretreatment of agricultural wastes, including rice straw, rice hulls, and sugar cane bagasse, processing the materials at temperatures of 210-220 deg C with and without acetic acid (Magara, 1989). Magara reported that samples of rice straw and bagasse were most effectively digested by cellulases after treatment and that operating temperatures could be lowered by 10-30 deg C with the addition of 0.5% acetic acid.

NASA STUDY (1993)

In 1993, Cullingford et. al., was issued a U.S. Patent on behalf of the National Aeronautics and Space Administration (NASA) for a method of pretreating a mixture of water, acetic acid and cellulosic waste products with microwave energy at high pressure in an autoclave. Cullingford's goal was to increase the enzymatic digestibility for converting the waste into soluble saccharides for use as a feedstock for ethanol or food protein in long duration space missions. (Cullingford 1993).

Pre-2000 Lignocellulosic Pretreatment Literature Summary

Much of the earlier work demonstrated that microwaves could rapidly heat solutions of lignocellulosic feedstocks to temperatures and pressures similar to that of conventional processes. As part of this effort, the researchers hoped that the rapid heating and perhaps selective heating of microwave of lossy¹ materials within the lignocellulosic matrix would induce structural transformations that would improve the total yield and efficiency of the process. Data to support this latter hypothesis were inconclusive.

POST-2000 LIGNOCELLULOSIC PRETREATMENT LITERATURE

Coincident with the beginning of the new millennium and the more intense search for alternative energy sources, and biofuels in particular, more recent literature has been reported on the subject.

¹ A lossy material is a term used to describe a microwave absorbing material.

China and Sweden Research (early 2000s)

Kunlan et. al (China) reported on the use of microwave energy and metal halides (such as sodium chloride, lithium chloride, potassium chloride, etc.) to accelerate the rate of hydrolysis of soluble starch to D-glucose (Kunlan, 2001). Kunlan attempted to exploit the microwave-induced current flow of the salt solution to enhance the starch to sugar conversion process. He compared his microwave data to the same solutions heated up to 145 deg C in a hot oil bath and reported that the rate of reaction was significantly (100x) higher using microwave. Kunlan attributed the higher reaction rates to local superheating of the salt solution due to the coupling of the microwave with the metal halide. Palm et. al (Sweden) describes the extraction of hemicellulosic oligosaccharides from spruce, using microwave or steam treatment (Palm, 2003). Palm reported that microwave treatment at induced temperatures of 200 deg C for five minutes in enclosed vessels resulted in greater hemicellulose yields than that induced at similar temperatures using steam treatment.

Thai Research (2003)

Kitchaiya (Thailand) was one of the first researchers to investigate the use of microwave energy under atmospheric conditions using a novel strategy to create superheated, high temperature conditions at atmospheric pressure (Kitchaiya, 2003). This was accomplished by immersing ground rice straw in a water- glycerine solution, which depressed the vapor pressure of the mixture compared to water-alone straw. This permitted Kitchaiya to achieve processing temperatures of 200 deg C without boiling off the solution, resulting in enhanced enzymatic saccharification. Kitchaiya reported that such processing was as effective as steam explosion due to the high temperatures achieved in his atmospheric process.

Chinese Research (2006, 2010)

Zhu et. al (China), who also experimented at atmospheric conditions, examined the affect of microwave-alkali (sodium hydroxide) pretreatment on the enzymatic hydrolysis of rice straw, building upon the earlier work of Chinese researchers (Zhu, 2006). He found that pretreating alkali-rice straw solutions with microwave for six minutes, using power levels ranging from 300-700W, induced a much higher initial hydrolysis rate than that induced by conventional boiling of the solution. The total rice straw sugar yield, however, remained the same. Zhu also reported that microwave energy used for heating the enzymatic solution to maintain a 45-55 deg C temperature had an adverse effect, lowering the rate of hydrolysis and the total yield.

Li et. al (Li 2010) reported on modeling work undertaken at the Materials Science and Engineering School in Changsha, Hunan in China that was developed to estimate the pressures and temperatures that would be necessary to introduce major disruption in wood cells due to microwave heating. The results suggest that temperatures in excess of 168 deg C would be required to induce such an effect.

U.S. Research (2007, 2008)

Keshwani et. al. (Keshwani 2007) reported on work undertaken at North Carolina State University in which switchgrass was exposed to low power levels of microwave (125-1250W) in water and dilute alkali (NaOH) and dilute acid (H₂SO₄) solutions. Keshwani was investigating whether such pretreatment could increase the rate of enzymatic hydrolysis (production of sugars). Keshwani reported that the most efficient method for using microwave was with alkali at the lower range of power levels (250 W) to avoid charring of the biomass. While the data reported showed some minor improvement in sugar production when compared to conventional treatment, Keshwani emphasized the rapid increase in processing rates (10 minutes using microwave versus 60 minutes using conventional heat to achieve equivalent levels of hydrolysis) as the major observable benefit.

Hu and Wen (U.S.) at Virginia Tech reported on the successful use of microwave energy to enhance enzymatic digestibility by comparing the use of microwave heating versus conventional heating of water-soaked switchgrass processed at 190° C for 30 minutes (Hu, 2008). Hu and Wen also found that that addition of alkali could further enhance the digestibility. By studying scanning electron microscopic images before and after treatment, Hu was able to differentiate structural changes to the switchgrass and attributed it, at least in part, to the selective heating of the lossy part of the lignocelluloses. He attributed the observed disruption of the recalcitrant structure of the biomass as a factor in enhancing enzymatic digestibility.

Post-2000 Lignocellulosic Pretreatment Literature Summary

In many of these post-millennium studies, researchers began to look at more unique ways to employ microwave energy. Kunlan's addition of salt to catalyze the starch to sugar process, Kitchaiya's use of a water-glycerine mix to provide for high temperature processing at atmospheric pressures, and Zhu's basic examination of the performance at atmospheric conditions were designed to investigate alternatives to high pressure processing of lignocellulosic feedstocks. These approaches were driven by the realization that from a practical standpoint the benefits of microwave energy, if they exist, would not be realized as a substitute heat source in high temperature and pressure reactors, but by employing microwave in a manner that takes advantage of one or more of the unique characteristics of the radiation to minimize or eliminate the need and cost associated with aggressive processing conditions.

Hu and Wen (Hu 2008) arguably provided the most convincing data to suggest that microwave radiation could enhance the process beyond that of conventional heat sources, however it is of note that the deployment of industrial microwave equipment at the scale necessary to achieve commercial processing conditions (in highly pressurized reactors) has not been demonstrated. All of the reported studies were undertaken in lab scale microwave ovens. This latter point is critical. Scale up of microwave applicators from small laboratory ovens to commercial-sized equipment is not a straightforward process and employing microwave energy in "high-pressure reactors" to achieve the thermo chemical conditions necessary to enhance feedstock enzymatic digestibility will require the design of systems that as of this date do not exist, and will be costly to fabricate and operate.

POST-2000 STRUCTURAL EFFECTS LITERATURE

Prior research has shown that microwave energy can induce structural transformations in a lignocellulosic matrix at atmospheric conditions by penetrating and interacting (directly or indirectly) with the lossy materials (primarily moisture) within lignocellulosic structure. Most of the studies where these transformations were reported were not interested in enhancing the enzymatic susceptibility of cellulosic materials to saccharification. They were focused on alternative objectives that included 1) the effect of microwave drying on the strength characteristics of structural wood, 2) the use of microwave to induce fiberization (break up the fibers) of the wood product to reduce pulping energy costs, and 3) the application of microwave to increase the permeability and pore space of wood beams to provide improved preservative penetration into the beam.

Drying: Swedish (2003), Iranian (2007), Portugese (2006) Research

Hansson and Antti (Sweden), performing drying experiments in a domestic microwave oven with 1.4 kW of power, reported no differences in wood strength measurements between microwave drying and conventional drying (Hansson 2003). Taskini (Iran) compared the effects of using convectional air drying, microwave drying (1 kW oven), and infrared drying on the strength of Guilan spruce woods in Iran. The experimental results showed that microwave drying time was significantly reduced, while the strength stays higher than that obtained in convectional and infrared drying. (Taskini 2007). While Hansson and Taskini reported no structural degradation of wood when exposed to microwave drying, Machado (Portugal) reported significant degradation in the strength of oak wood when using microwave energy compared to that of conventional heat sources in a 550 kW oven (Machado, 2006).

Pulping: Oak Ridge National Laboratory Research (2002)

Scott (U.S.) investigated the use of high-power (20-50 kW) microwave energy in a commercial microwave facility to pretreat black spruce logs for paper production. His objective was to alter the structure of the wood so that fiberization would occur more easily, thereby reducing mechanical pulping energy requirements (Scott 2002). Scott observed that during high-power treatment the logs were quickly heated and considerable steam pressure was released, causing extensive internal fracturing. Scott reported up to 15% energy savings as a result of the pretreatment process.

Permeability and Void Space: Australia (2002, 2004)

Vinden et. al. (Australia) was issued a U.S. Patent on a method to increase the permeability of wood logs using high-powered microwave (Vinden 2004). Vinden in his patent reported that the pore space, permeability and the structural integrity (mechanical moduli) of wood logs and large chips can be significantly altered, by several orders of magnitude, by high-powered microwave pre-treatment, and that such processing facilitates the injection of amendments (preservatives) into the internal structure of the wood. Torgovnikov and Vinden reported that under microwave induced internal pressures the pit membranes in cell walls, tyloses in vessels, and the weak ray cells are ruptured to form pathways for easy transportation of liquids and vapors throughout the wood structure (Torgovnikov 2002).

Post-2000 Structural Effects Literature Summary

Prior studies on the effects of microwaves on the lignocellulosic structure, as reported above, show significant differences among researchers, insofar as wood transformation and or degradation is concerned. Some report wood degradation and others do not. These differences could be attributed to a number of factors that were not carefully controlled or monitored during much of the reported research. Some of these factors could include: the 1) sample moisture content (dried, resaturated or green,), 2) sample size (dimensions and surface area to volume ratio) and 3) the applied microwave power density (kW per mass).

EXPERIMENTAL OVERVIEW

The experimental process was divided into three test stages, each of which was defined by the relative available power in the microwave applicator used in the process. These stages included:

1. Low Power Testing,
2. Medium Power Testing,
3. High Power Testing.

The general analytical strategy involved in the evaluation included:

- The preparation of selected feedstock samples (size, moisture content and amendment addition)
- Exposure of the feedstock samples to microwave energy in one or more of the available applicators for selected durations
- The conduct of extraction tests after microwave pretreatment to quantify solids and/or hemicellulose extraction, or glucose production (enzymatic hydrolysis) of the pretreated samples. The results were compared to control samples that were comprised of hot water treated samples or untreated samples to assess the relative microwave effects.

Table 1 provides a tabular overview of the three stages.

1. LOW POWER TESTING

During **the low power** testing stage:

- Maple wood chips ($\frac{5}{8}$ to $1\frac{7}{8}$ inches in size) were processed in two ~ 1 kW applicators: a domestic Sharp oven and a laboratory Milestone Reactor. The Milestone Reactor was capable of achieving superheated processing conditions by microwaving the chips in enclosed reactors
- The moisture content of the chips was adjusted to saturated (referred to as high solids content samples) and supersaturated (referred to as low solids content samples) conditions prior to testing. This was done to determine whether moisture content had any effect on the efficiency of microwave pretreatment
- Amendments (acetic acid and sodium chloride) were added separately and in combination to assess whether they could induce measurable benefits
- Treatment times varied from 60 to 120 minutes in pressurized vessels for saturated moisture samples; high solids samples were processed for five minutes
- For open vessel testing, the processing time was limited due to drying and subsequent scorching of the samples. To compensate for this in the low solids tests, moisture was periodically introduced into the sample. In the high solids tests, processing times were limited to avoid scorching

- Microwave performance was evaluated by comparing the microwave results to hot water extractions in an MK digester (a pressurized reactor), which was used as a control.

All test runs were assessed by measuring the loss of woody mass (solids loss) after treatment, and hot water extraction. The use of solids loss as an indicator test is based on the assumption that hot water solubility of lignin and cellulose are relatively low, therefore most of the solids lost during the treatment is expected to be hemicellulose.

2. MEDIUM POWER TESTING

During the **medium power** testing stage:

- Green willow logs were used and were processed in a 3.2 kW multi-modal microwave cavity for periods of 36 seconds to 120 seconds
- Two sets of logs were used that included 3- and 6-inch long samples, each respectively with $\sim 1\frac{1}{2}$ - inch diameters. The 6-inch long samples had approximately twice the mass of the 3-inch long samples. In this manner, with a constant applied power of 3.2 kW, it was possible to examine whether differences in extraction or strength could be observed with a doubling of the power density
- All tests were done at atmospheric pressure conditions
- After microwave treatment, alkali (sodium hydroxide) was used to extract hemicellulose from the treated willow and the extracts were analyzed for hemicellulose (xylan)
- The microwave results were compared to untreated control samples
- The compressive strength of 6-inch samples that were processed were also tested to assess whether steam explosions within the willow wood structure could be induced by rapid internal heating of moisture in the wood structure, by microwaves, and whether such explosions could open the pore structure of the biomass
- Two potential benefits were envisioned: 1) enhancement of hemicellulose extraction and 2) reduction of the wood strength. Biomass preprocessing normally includes a milling step. Milling is an effective but costly way to increase the extraction of hemicellulose from lignocellulosic biomass. It is well known that mechanical pulping of wood at higher temperatures leads to a reduced consumption of pulping energy due to a softening of the wood. The goal in this case was to establish whether microwave treatment could reduce the strength of the woody mass and perhaps reduce milling energy requirements.

Table 1. Experimental Program Overview

Test Stage	Applicator(s)	Sample(s)	Sample Preparation	Test Conditions	Analysis
Low Power	1 kW Sharp Oven 1 kW Milestone Reactor	Maple Chips	Moisture saturated and supersaturated samples With and without amendments (NaCl and HAC)	Pressurized (Superheated conditions) Atmospheric pressure conditions	Hot water solids extraction
Medium Power	3.2 kW Multimode Cavity	Willow logs	Green samples Surface area (A) to volume (V) ratio adjustments (A/V) for power density modifications	Atmospheric pressure conditions	Alkaline extraction - hemicellulose content Compressive strength
High Power	25 kW resonant cavity applicator 100 kW traveling wave applicator	Willow logs	Green samples Surface area (A) to volume (V) ratio adjustments (A/V) for power density modifications	Atmospheric pressure conditions	Hot water solids extraction Pre-milling followed by hot and cold water extraction and enzymatic hydrolysis - glucose production No milling - just hot and cold water extraction followed by enzymatic hydrolysis - glucose production Pre-milling followed by cold water and alkaline extraction and enzymatic hydrolysis - glucose production
	25 kW resonant cavity applicator	Pine logs	Green samples Surface area (A) to volume (V) ratio adjustments (A/V)	Atmospheric pressure conditions	Hot and cold water extraction followed by milling and enzymatic hydrolysis - glucose production Hot and cold water extraction followed by milling and enzymatic hydrolysis - glucose production
	25 kW resonant cavity applicator	Maple Chips	Moisture saturated sample	Atmospheric pressure conditions	Hot water extraction followed by solids loss measurements Cold water alkaline extraction followed by solids loss and ethanol precipitate loss

3. HIGH POWER TESTING

During the **high power** testing stage:

- Two applicator types and three feedstock sources were used in the evaluation. The two applicators employed included: 1) a 20 kW, 2450 MHz, variable power, resonant cavity applicator, and 2) a 100 kW, 915 MHz, variable power, traveling wave applicator. The three feedstock sources included small willow wood logs, pine logs and maple chips
- Willow logs were treated using the 20 kW, 2450 MHz applicator with applied power up to 15 kW, and the 100 kW, 915 MHz applicator with applied power up to 40 kW
- Pine and maple feedstocks were treated with the 20 kW, 2450 MHz applicator at power levels up to 15 kW
- Two sets of green willow and pine logs were used in the high power testing (i.e., the 3- and 6-inch long samples, each respectively with $\sim 1\frac{1}{2}$ - inch diameters)
- Maple chips were adjusted to moisture saturated conditions
- All tests were done at atmospheric pressure conditions
- Several different extraction procedures were used to assess the benefits of treatment, as listed in Table 1. A more detailed description of these procedures is presented in the high power testing section of the report.

LOW POWER APPLICATOR TESTING

PRIMARY OBJECTIVE

The primary objective of the low power tests was to determine if the exposure of a lignocellulosic feedstock (maple wood chips) to low power microwave radiation in pressurized and unpressurized vessels, and, with or without selected amendments, could degrade the feedstock sufficiently to enhance the extraction of hemicellulose from the feedstock above levels achievable using conventional hot water extraction methods.

GENERAL APPROACH

To undertake this effort, a series of specially designed tests was designed using maple wood chips and low power microwave applicator equipment, described below. Tests were conducted in both pressurized vessels where superheated steam could be generated and in non-pressurized vessels, where steam was vented to the atmosphere. The maple wood chips were moisture conditioned prior to microwave exposure, and also amended with acetic acid (HAc) and sodium chloride (NaCl).

TEST EQUIPMENT

Open vessel or non-pressurized testing was conducted in open beakers using a 1 kW Sharp domestic microwave oven, equipped with a glass carousel.

Pressurized vessel testing, also referred to as closed vessel testing were conducted using an Ethos TC laboratory microwave unit manufactured by Milestone, a manufacturer of microwave laboratory systems. A photograph of the Ethos unit is shown in Figure 1.

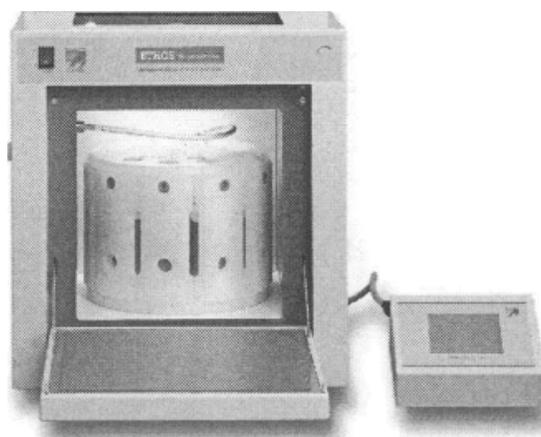


Figure 1. Ethos Microwave Oven

The Ethos oven consists of two, 800-watt industrial magnetrons, each with its own high voltage power supply, resulting in 1,600-watt of microwave installed power. Delivered power is approximately 1000-watts. Samples are placed in sealed Teflon vessels (10 vessels are available for testing in the subject system), which are placed onto a rotating table (or body). Each vessel contains a total volume of 100 ml. Internal vessel pressures up to 100 bar (1450 psi) can be withstood. A temperature probe is outfitted in one of the 10 vessels. The Ethos controller maintains temperature by turning on and off microwave power to maintain the desired temperature profile.

Control tests (hemicellulose extraction of maple wood chips using conventional heating) were conducted using an MK digester.³ An MK Digester is a laboratory digester (e.g., pressure cooker) that is widely used in the pulp and paper industry to assess various chemical compositions, temperature, and pressure conditions to optimize and study the pulp and chip cooking process. It is suitable for both alkaline and acid digesting process with various types of wood chips and fiber sources.

TEST FLOW DIAGRAMS

The low power series of tests conducted are depicted in a testing flow diagram presented in Figure 2. The flow diagram is divided into six steps that define the experimental procedure used for each respective test and include:

1. Sample Type,
2. Sample Modification,
3. Moisture Conditioning,
4. Amendment Addition,
5. Microwave Pretreatment,
6. Extraction Methods.

The first two steps were common for all tests:

1. Sample Type

The lignocellulosic sample used was maple wood chips obtained from Northeastern sugar maple logs. The original logs with diameters ranging from 4- to 10-inches, in preparation for testing were debarked, chipped, screened (scalped) to pass a $1\frac{7}{8}$ inch diameter screen and be retained on a $\frac{5}{8}$ inch diameter screen (i.e., chips ranged in size from $\frac{5}{8}$ to $1\frac{7}{8}$ inches).

2. Sample Modification

After screening, the wood chips were air dried at SUNY ESF's Department of Paper and Bioprocess Engineering to prevent decay during storage.

³ Manufactured by M/K Systems, Inc of Bethesda, MD.

3. Moisture Conditioning

In the third step, water was added to the dried feedstock samples in two different amounts, and the testing procedures were split into two test lines (see Figure 2). Moisture conditioning was characterized by the resultant liquid to solids (L/S) ratio after moisture addition. The low solids tests were undertaken on samples with an L/S ratio of approximately 5:1 or approximately 80-85% moisture or 15 to 20% solids.⁴ The high solids tests were undertaken on samples with an L/S ratio of greater than 1:1 or approximately 10 to 50% moisture or 50 to 90% solids.

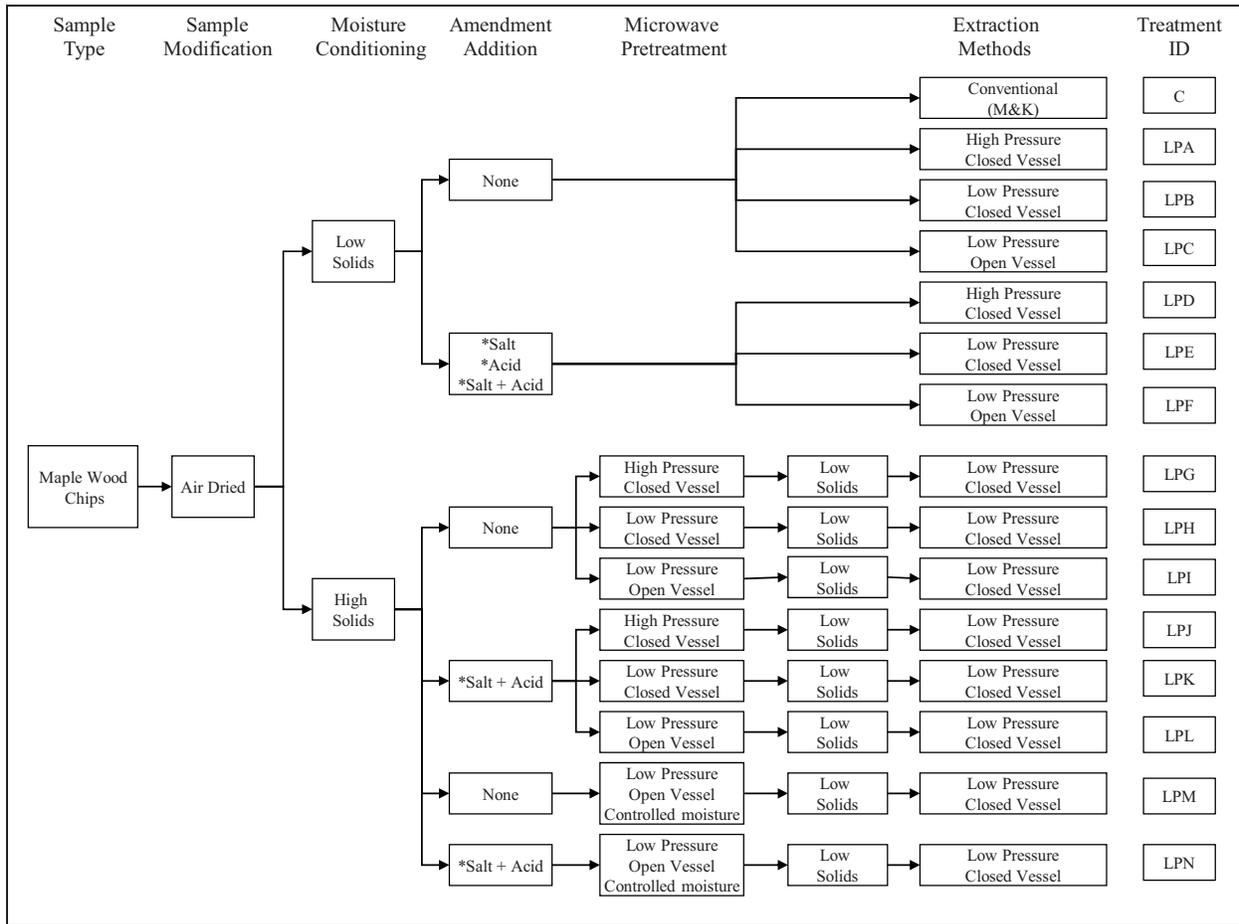


Figure 2. Low Power Microwave Testing Flow Diagram

⁴ Manufactured by M/K Systems, Inc of Bethesda, MD.

The low solids testing line used microwaves in a combined pretreatment and extraction step. As a pretreatment step, the feedstock was exposed to radiation that was used to preheat the conditioned wood chips (with and without amendments) and as an extraction step, the microwave was used to heat the excess liquor to extraction temperatures.⁵ As a result, in Figure 2, for low solids testing, the microwave pretreatment step is combined with the extraction step.

The high solids testing line was designed as a pretreatment strategy to assess whether the absence of excess moisture (and exposure of the feedstock to a higher power density) might induce some effect on the feedstock prior to extraction. As a result, in Figure 2, microwave pretreatment is shown as a separate pretreatment step. In the high solids extraction step, microwave was also used to heat excess liquor that was added to the sample prior to extraction.

4. Amendment Addition

In both the low solids and high solids test, amendments (acetic acid, and sodium chloride) were added to the liquor (water) that was added to the wood chips. The amendments were added in amounts designed to yield a 1% acetic acid and/or 0.05 M sodium chloride solution. Acetic acid is a naturally occurring acid generated by the cleavage of acetyl groups from hemicellulose during hot water extractions (autohydrolysis process). During the autohydrolysis process the acetic acid formed decreases the pH and aids in the hydrolysis of glucosidic bonds in the hemicellulose. Sodium chloride was added in an attempt to increase the conductivity of the liquid and induce a microwave-generated current in the amended liquor, similar to the reportedly successful of Kunlan in China (Kunlan, 2001).⁶

5. Microwave Pretreatment

During low solids testing (see Figure 3 and Item 3), the maple chips were exposed to microwave radiation in a combined pretreatment and extraction step. During high solids testing, the two steps (pretreatment and extraction) are shown in Figure 3 as separate steps. The high solids pretreatment step was performed in one of two types of reactors:

- Pressurized vessels (referred to as closed vessels in Figure 2), and
- Non-pressurized vessels open to the atmosphere (referred to as open vessels in Figure 2).

The closed vessel pretreatment test was used to increase the pressure and temperature to superheated conditions above 100 deg C while maintaining a saturated steam condition in the reactor.

⁵ All L/S sample ratios were adjusted to 5:1 ratios prior to the hot water extraction step in both the low and high solids test runs.

⁶ See Relevant Literature Section of this report.

The open vessel pretreatment test involved the development of special experimental procedures for applying microwave radiation to high solids, (moisture saturated chips) without driving off all the moisture and charring the wood chips during extended microwave application at atmospheric conditions. These test procedures are described below.

6. Extraction Methods

Low solids treatment, as noted above, consisted of an extraction at low solids using microwave energy while high solids microwave treatments consisted of microwave treatment at high solids followed by the addition of excess liquor and extraction, using microwave energy at lower solids content. The percent solids of the extraction solution (hot water) for both low and high solids extractions were 20 percent (5:1 liquor to wood ratio).

To simplify the experimental process during low power testing, the wood mass loss during extraction was used as an indicator of the mass of hemicellulose extracted. The use of solids loss as an indicator test is based on the assumption that hot water solubility of lignin and cellulose are relatively low therefore most of the solids lost during the treatment is expected to be hemicellulose.⁷ Wood mass loss was calculated by:

- a. Determining the oven dry weight of the chips prior to extraction (calculated as mass of chips multiplied by the solids content of the chips)
- b. Determining the mass of solids lost during the extraction process (calculated as oven dry weight before the extraction minus oven dry weight of the chips after extraction)
- c. Providing a correction factor for the mass of solids retained in the wood pore space⁸
- d. Calculating the relative mass loss (calculated as the difference in the masses of the sample before extraction and corrected mass after extraction divided by the oven dry mass of the sample before extraction).

LOW POWER TESTING AND RESULTS

Low power test procedures and test results are described in the following two sections. Each test is identified with a specific treatment identification code (ID) that is keyed to Figure 2. The data shown in each table represents the average value of the two tests conducted on each sample.

⁷ Measurement of the hemicellulose extracted directly requires the hydrolysis of polymers and oligomers to monomers and then analysis in a process that is very time consuming but was used in Medium Power Testing.

⁸ During extraction, mass is first dissolved in liquor close to or within the chip structure (void volume). The dissolved material within the chip will then diffuse to the liquor outside the chip. Washing can be used to easily remove the extract from the outside the chips, but the diffusion rate of extract from the void volume within the chip is dependent upon many factors including: chip size, permeability, liquor volume, etc. To compensate for solids that are soluble in liquor within the chips but has not yet diffused a corrected wood mass (CWM) was calculated [CWM = $EW_{Mod} - (EWM_{wet} - EW_{Mod}) * \%S_{ext} / (1 - \%S_{ext})$], where CWM is the corrected wood mass, EW_{mod} is the mass after drying, EW_{wet} is the mass before drying and $\%S_{ext}$ the nonvolatile solids content of the extract. $\%S_{ext}$ is used as a conservative estimate of the nonvolatile solids content within the void spaces. It is expected that the actual content will be higher, as diffusion limitations will likely lead to a buildup of solid within the void spaces. The non-volatile solids content of the extract ($\%S_{ext}$) was measured gravimetrically by oven drying at 105°C. The extracted wood was drained and weighed to get the mass before drying (EW_{wet}) and after oven drying at 105°C (EW_{dry}).

Control Tests (Treatment ID: C)

Control tests were performed in the previously described M&K digester. Approximately 425g of maple wood were loaded into the digester and water was added at a liquor to wood ratio of 5:1. The samples were then brought to the extraction temperature, which ranged from 100°C to 160°C and held at temperature for two hrs. The extract was then blown through a condenser/heat exchanger to reduce the heat to below 60°C. The extracted wood chips after draining were weighed and dried for analysis.

Table 2. Low Solids Control Tests (M8K Digester)¹

Sample ID	Temp (deg C)	Solids Loss (%)
C	100	1.2
C	120	2.1
C	140	6.4
C	150	13.4
C	160	25.8
1.All tests were conducted at L/S ratios of 5:1 and extraction times of 120 min.		

The results presented in Table 2 show that solids loss during the control tests ranged from 1.2% at a 100°C processing temperature to 25.8% at a 160 deg processing temperature.

Low Solids Closed Vessel (Treatment ID: LPA, LPB, LPD, LPE)

Closed vessel testing was undertaken by loading approximately 4 g of air-dried maple wood chips into four of the Milestone microwave reaction vessels. Approximately 20 g of liquor was added to the vessels. During the test runs with amendments (ID: LPD, LPE) either one percent acetic acid (HAc) or 0.05M sodium chloride or both were added to the liquor. The loaded vessels were sealed and microwave heated. The desired temperature profile was set with a six min heat up time to temperature (100°C to 160°C) and then reaction for the desired time (60 or 120 min) at temperature. The temperature was controlled at the set profile by on-off cycles which generally resulted in peaks ~-1°C and +5°C around the set profile. After the reaction, the reactors were allowed to cool to below 60°C before removal. The samples that were processed at 100°C were designated as low pressure closed vessel samples. Two samples were tested by draining and then drying the chips, and a sample of the extract was collected to determine the mass of the remaining chips and the percent of non-volatile solids in the extract.

**Table 3. Low Solids Closed Vessel Testing (Ethos)
No Amendments¹**

Sample ID	Temp (deg C)	Time (min)	Solids Loss (%)
LPB	100	120	1.5
LPA	140	120	5.1
LPA	160	60	12.2
1.All tests were conducted at L/S ratios of 5:1.			

The results of closed vessel testing without amendment addition, presented in Table 3, show that solids loss during the low solids closed vessel testing ranged from 1.5% at a 100°C processing temperature to 12.2% at a 160°C processing temperature. The results were judged similar to the control tests (see Table 2), with the exception being the 25.8% solids loss during the control tests at 160°C vs. the 12.2% loss using closed vessel microwave processing. This difference was attributed to the 60 minute processing time of the microwave test versus the 120-minute processing time of the control test.

The addition of amendments, the results of which are presented in Table 4 provided some marginal increase in solids extraction (e.g., HAc at 140°C), but the results were not sufficiently dramatic to draw any conclusions.

**Table 4. Low Solids Closed Vessel Testing (Ethos)
With Amendments¹**

Sample ID	Temp (deg C)	Time (min)	Amendment Addition	Solids Loss (%)
LPE	100	120	1% HAc	1.4
LPD	140	120	1% HAc	8.2
LPE	100	120	.05M NaCl	1.3
LPD	140	120	.05M NaCl	5.5
LPE	100	120	1% HAc & .05M NaCl	1.2
LPD	140	120	1% HAc & .05M NaCl	1.9
1.All tests were conducted at L/S ratios of 5:1.				

Low Solids Open Vessel (Treatment ID: LPC, LPF)

Low solids (high moisture content) hot water extractions were conducted in the Sharp 1 kW microwave were conducted in open containers at a liquor to wood ratio of approximately 5:1. A 20 g (oven dry equivalent) sample of maple wood chips was placed in a 250 ml beaker with 100 ml of extraction liquor. For amendment testing, one percent acetic acid (HAc), 0.05M sodium chloride (NaCl) and a blend of HAc and NaCl were added based on the liquor mass [LPF]. The beaker was then placed on the center of the glass carousel and microwaved on high for 120 min. During the experiment, hot water was added every 15 minutes to replace moisture lost due to evaporation and to maintain the appropriate liquor level. After the extraction, the chips were drained and a portion was dried along with a sample of the extract to determine the mass loss. A single sample was treated at each of the reported conditions.

The results shown in Table 5 show some increase in solids extraction at 120°C and 120 minutes with both HAc and NaCl addition, but the results were not sufficiently dramatic to draw any conclusions.

**Table 5. Low Solids Open Vessel Testing (Sharp)
With and Without Amendments**

Sample ID	Temp (deg C)	Time (min)	Amendment Addition	Solids Loss (%)
LPC	100	120	None	1.4
LPF	120	120	1% HAc	1.3
LPF	100	120	.05M NaCl	1.2
LPF	120	120	1% HAc & .05M NaCl	1.6

High Solids Closed Vessel Pretreatment (Treatment ID: LPG, LPH, LPJ, LPK)⁹

Closed vessel treatment was conducted in the 1.6 kW Ethos oven. Four gram (oven dry equivalent) samples of moisture conditioned maple wood chips were placed in the sealed reaction vessels and subjected to microwave energy under temperature control (between 100°C to 200°C) for a total time of five minutes including heat up and time at temperature. Microwave energy was controlled by a temperature probe in the top of one of the vessels. After reaching temperature, the microwave was turned on and off to maintain temperature. The time required to heat the chips to the desired temperature was recorded. After pretreatment, the chips were allowed to cool to less than 70°C prior to low solids microwave extraction at 100°C for 120 minutes. The average values of two processed samples were reported for each condition.

⁹ During high solids testing, before microwave treatment, samples of air-dried maple wood chips were brought to moisture contents of 7% by mass and saturated or approximately 50% by mass. The air-dried samples had a moisture content of 7% and needed no conditioning. To saturate chips a weighed sample of air-dried chips was placed in excess liquor, and vacuum was applied overnight to allow for better saturation of the chips and removal of water. Samples that were treated with added amendments had amendments added to the liquor based on mass of the liquor before saturation of the chips. After saturating the chips with liquor, the chips were drained for 15 minutes to remove excess liquor before microwave testing.

The results of the high solids, closed vessel five minute microwave pretreatment tests are presented in Table 6. The results of these studies yielded more positive results than the prior low solids tests. The increased solid loss was marginal for the lower temperatures but became significant for the 200°C treatments increasing to 7.2%, 9.7%, and 20.24% for saturated chips, 7% moisture chips, and chips saturated with acetic acid/ sodium chloride liquor respectively. The results suggest that temperatures must reach close to 200° F before significant degradation occurs in the lignocellulosic structure, and in this temperature range amendments begin to play a more prominent role in the process. This is more readily seen in Figure 3. Closed Vessel, High Solids Pretreatment Test Data Graph, which is a graphical representation of the data from Table 6.

High Solids Open Vessel Pretreatment (Treatment ID: LPI, LPM, LPL, LPN)

High solids pretreatments in open vessels were conducted using the 1kW Sharp microwave oven. Four grams (oven dry equivalent) of saturated maple wood chips were paced in a glass beaker and microwaved at a power setting of full or 50%.¹⁰ To determine the time that the samples would be treated, pretesting was done with additional samples of pretreated chips. The pretested chips were microwaved until the chips started to show scorching, and after a series of three tests, the time that would be used on samples was set at 90% of the average scorching time. After pretreatment, samples were cooled and bagged in preparation for extraction processing. All samples were saturated prior to testing, as described previously, and after an initial treatment, some samples were re-saturated with water and then treated a second or third time to allow for more microwave energy while maintaining moisture content. Samples were then cooled and bagged.

The pretreated maple wood chips were extracted in the milestone sealed vessels at a 5:1 liquor to wood ratio. Samples were heated to 100°C over six minutes and then maintained at temperature for two hours. After the extraction, the vessels were allowed to cool to less than 70°C. The extract was then drained from the chips and the chips and a sample of extract used to calculate the mass loss.

¹⁰ During high solids open vessel testing, temperatures in the solution were not measured and microwave exposure was monitored by recording the power setting, duration, and the initial temperature.

**Table 6. High Solids Closed Vessel Testing (Ethos)¹
With and Without Amendments**

Sample Number	Sample ID	Temp ² Deg C	Heat Up ³ (Sec)	Moisture Conditioned	Amendment Addition	Solids Loss ⁴ %
1	LPH	100	30	Saturated	None	1.8
2	LPG	150	45	Saturated	None	1.8
3	LPG	200	104	Saturated	None	7.2
4	LPH	100	45	7%	None	2.0
5	LPG	150	70	7%	None	1.6
6	LPG	200	111	7%	None	9.7
7	LPK	100	31	Saturated	1% HAc & .05M NaCl	2.3
8	LPG	150	50	Saturated	1% HAc & .05M NaCl	2.8
9	LPG	200	110	Saturated	1% HAc & .05M NaCl	20.2

1. High Solids pretreatment conducted at saturated conditions (L/S ratio of 1:1) or at 7% moisture.
2. Pretreatment temperatures
3. Total pretreatment time including startup time was 5 minutes for each test including heat-up period.
4. Solids loss after 120 minutes of extraction at 100 deg C.

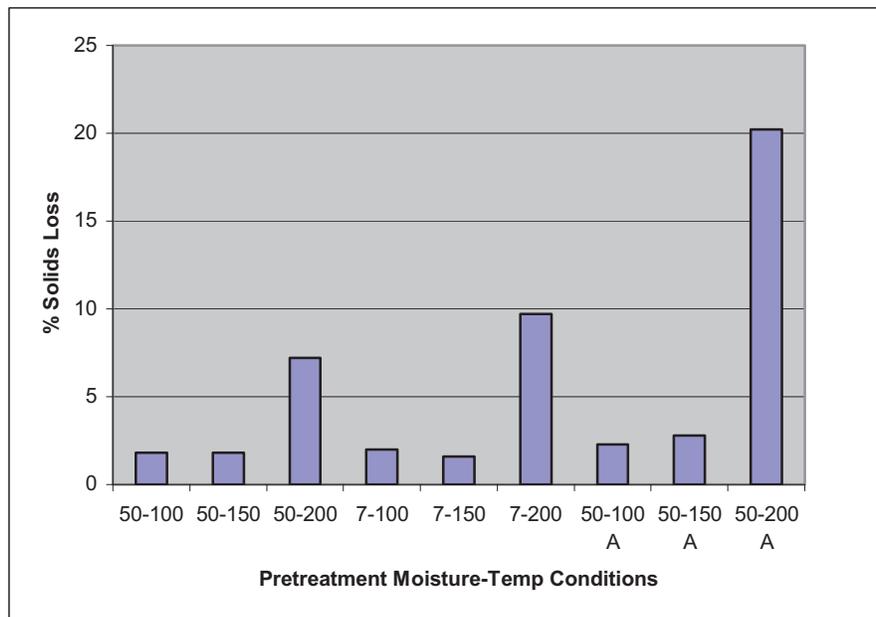


Figure 3. Closed Vessel, High Solids Pretreatment Test Data Graph

The results of the high solids open vessel testing for individual tests are presented in Table 7. Open vessel moisture pretreatments showed little difference in the amount of solids that were extracted from the chips, regardless of the power setting, after a second or third treatment, whatever the initial temperature, and with or without amendments. Conditions were not sufficiently aggressive to breakdown the lignocellulosic structure.

**Table 7. High Solids Open Vessel Testing (Sharp)
With and Without Amendments**

Sample	Power Setting	Initial Temp	Moisture	Amendment	# of Treatments	Solids Loss
ID	I kW Oven	deg C	Conditioned	Addition		%
LPI	full	20	Saturated	None	1	2.5
LPM	full	20	Saturated	None	2	2.4
LPM	full	20	Saturated	None	3	3.1
LPI	full	100	Saturated	None	1	2.4
LPI	50%	20	Saturated	None	1	2.4
LPL	full	20	Saturated	1% HAc & .05M NaCl	1	2.3
LPN	full	20	Saturated	1% HAc & .05M NaCl	2	2.6
LPN	full	20	Saturated	1% HAc & .05M NaCl	3	--
LPL	full	100	Saturated	1% HAc & .05M NaCl	1	2.3
LPL	50%	20	Saturated	1% HAc & .05M NaCl	1	2.5

MEDIUM POWER TESTING

PRIMARY OBJECTIVE

The primary objectives of the medium power tests was to determine if medium power application could be used to open the structure of woody biomass samples and enhance the extraction of hemicellulose (reduce sample recalcitrance), compared to conventional alkali extraction. Additional tests were undertaken to determine whether the mechanical properties of the radiated samples could be impacted by microwave processing, and affect both the extraction data and the strength of the processed samples.¹¹

GENERAL APPROACH

To achieve the aforementioned objectives, willow stems were processed in a 3.2 kW commercial microwave oven. Processed samples were subjected to extraction and tested for hemicellulose content as well as compressive strength before and after microwave treatment.

TEST EQUIPMENT

Medium power tests were conducted using variable power 3.2 kW oven fabricated by Microwave research and Applications of Laurel, MD, using specifications defined by Thermex-Thermatron. The unit, which employs four mode stirrers, and contains a 21" x 13" x 9 7/8" cavity was designed to enable uniform distribution of application of microwave energy to the samples at higher power settings. A photograph of the 3.2 kW unit is shown in Figure 4.



Figure 4. 3.2 kW Cavity Applicator

¹¹ The examination looked at whether steam explosions within the wood structure, induced by rapid internal heating by microwaves, could open the pore structure resulting in two potentially beneficial effects: enhance hemicellulose extraction and reduce the wood strength. Biomass preprocessing normally includes a milling step. Milling is an effective but costly way to increase the extraction of hemicellulose from lignocellulosic biomass. It is well known that mechanical pulping of wood at higher temperatures leads to a reduced consumption of energy due to a softening of the wood.

Microwave treated and control samples were tested for compressive strength to determine the effects of microwave treatment on the mechanical properties of the sample. Compressive strength testing was undertaken at the Department of Civil Engineering at New York University-Polytechnic in Brooklyn, N.Y. Testing was undertaken using a Instron 8800 Fatigue Testing Machine. A photograph of the machine is shown in Figure 5



Figure 5. Compressive Strength Testing Machine

TEST FLOW DIAGRAMS

The medium power series of tests conducted are depicted in a testing flow diagram presented in Figure 6. The flow diagram is divided into five steps that define the experimental procedure used for each respective test and include:

1. Sample Type

Lignocellulosic samples used in medium power testing were approximately 1¹/₂-inch diameter willow stems harvested from SUNY ESF shrub willow plantations located in Central New York.

2. Sample Modification

Willow stems were cut to a length of either 3- or 6-inches resulting in two samples sets with different masses. The two sets included 3- and 6-inch long samples, each respectively with 1¹/₂- inch diameters. As a result, the 6-inch long samples had approximately twice the mass of the 3-

inch long samples. In this manner, since constant power was applied at 3.2 kW during exposure, it was possible to examine whether differences in extraction or strength could be observed with doubling of the power density.¹² All samples were stored in a frozen state until testing.

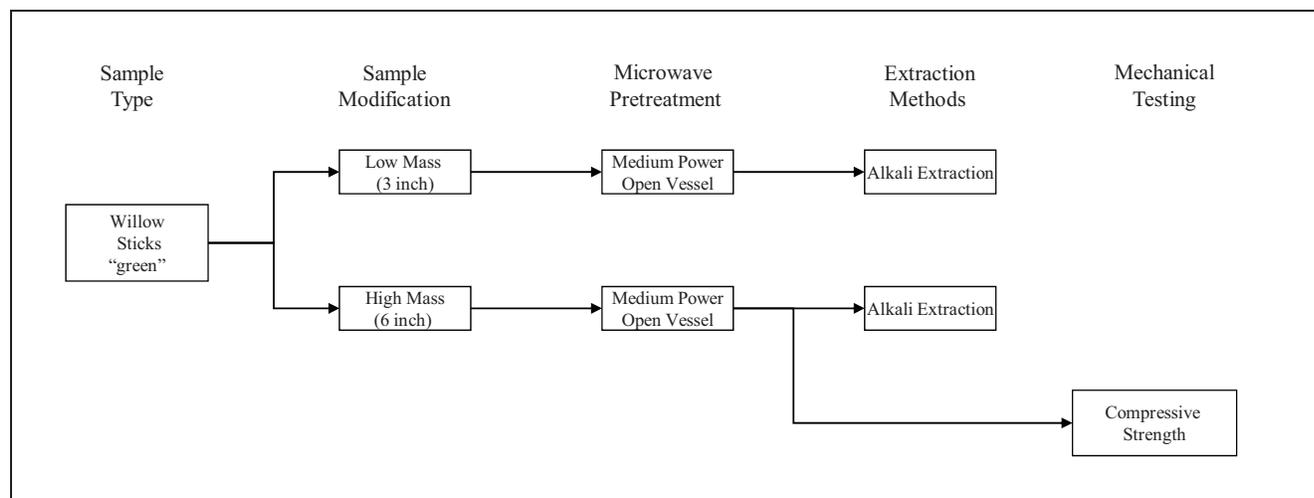


Figure 6. Medium Power Microwave Testing Flow Diagram

3. Microwave Pretreatment

All samples were radiated at 3.2 kW. The 3-inch samples were exposed to the microwave for 27 to 90 sec bursts and the 6-inch samples were exposed for a period of 36 to 150 sec. The exposure periods were limited by drying and eventual combustion of the samples. Sample weights were recorded before and 60 sec after microwave treatment to calculate moisture loss during treatment.

4. Extraction Method

Microwave treated and control (untreated) samples were debarked and cut into 1-inch long disks. Each disk was then quartered to form four wedges. Two wedges from each sample were oven dried to find the moisture content. Three wedges were stacked inside a 50mL centrifuge tube and a 4N NaOH solution was added in a 3:1 liquor to wood ratio, which filled the tube. The tubes were then placed in a 50°C incubator under rotation for 24 hrs. After extraction, the alkali extract was drained from the wedges and analyzed for xylan content. Proton nuclear magnetic resonance spectroscopy (¹H NMR) analysis was used to find the relative concentration of xylan in the extract. To 1ml of extract sample was added an internal standard of TSP. The TSP peak in each sample was calibrated to 90 and shifted to zero ppm. A chemical peak from xylan oligomers was located at 4.1 was integrated for each of the samples.

¹² The treatment of the 3-inch long samples at 3.2 kW results in an application rate of twice the power density (due to its one-half mass) over that of the 6-inch long samples.

5. Mechanical Testing

Mechanical testing was undertaken by exposing twelve, 6-inch long willow samples to 3.2 kW of power for 120 seconds. Three samples tested were not treated and used as controls. Three samples were tested immediately (within 15 minutes) after exposure, three samples at four hr after exposure, three samples at 24 hr after exposure and three samples at 48 hr after exposure.

MEDIUM POWER TESTING AND RESULTS

Sample Drying

During processing, the willow samples were subjected to microwave energy that rapidly (within seconds) converted the moisture present in the wood into steam. This resulted in rapid sample drying. The extent of drying was found, as expected, to be near linear to the applied energy input. Moisture loss data for each willow sample tested is listed in Table 8. A graphical representation of the moisture loss-energy data is shown in Figure 7. Above 2000 kJ/kg applied energy, the loss of mass was roughly equivalent the moisture content of the chips (chips dried), which was approximately 45% moisture.

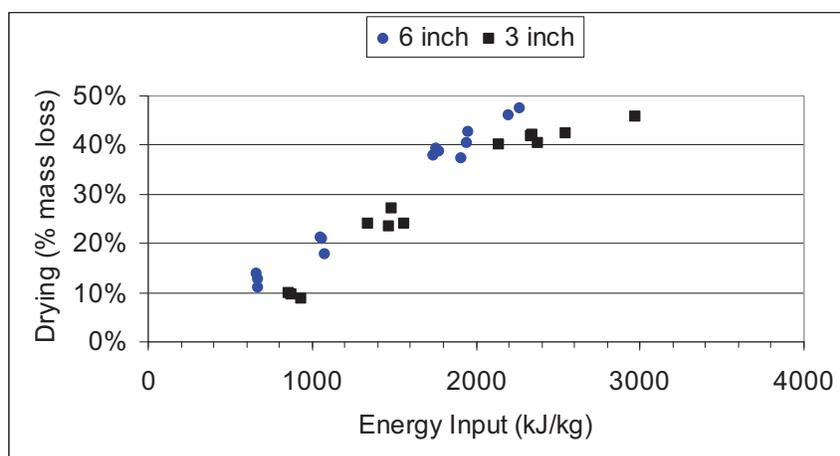


Figure 7. Drying of willow sticks during microwave processing

Alkali Extraction

The relative concentration of xylan (i.e., hardwood hemicellulose) in the extract was determined through ^1H NMR. The results are presented in Table 9. As shown in Figure 8, the control sample extract was found to have more xylan than extracts from the treated samples. This suggests that the application of microwave energy increased, rather than decreased the recalcitrance of the sample. The reduced extractability is likely due to changes in the wood that take place due to the drying of the wood, possibly due to “softening” of the lignin and its re-distribution to the fibril surfaces.

Table 8. Moisture loss from microwave treated willow sticks.

Sample¹	Sample Diameter (in)	Microwave Exposure Time (s)	Initial Weight	Final Weight	Moisture Loss (% of Initial wt)	Power Density Per Initial Wt (kW/kg)	Applied Energy (kJ/kg)
WS-20	6	36	173.8526	149.94	13.8%	18.41	663
WS-19	6	36	172.7817	153.98	10.9%	18.52	667
WS-13	6	36	171.6686	150.08	12.6%	18.64	671
WS-17	6	60	182.1318	143.638	21.1%	17.57	1054
WS-11	6	60	181.2137	143.08	21.0%	17.66	1060
WS-14	6	60	177.6000	145.9	17.8%	18.02	1081
WS-8	6	100	183.9630	114.449	37.8%	17.39	1739
WS-6	6	100	181.9514	110.534	39.3%	17.59	1759
WS-4	6	100	180.2305	110.36	38.8%	17.76	1776
WS-5	6	100	167.1030	104.93	37.2%	19.15	1915
WS-12	6	100	164.4278	97.83	40.5%	19.46	1946
WS-2	6	120	196.9519	113.16	42.5%	16.25	1950
WS-3	6	120	174.5531	94.28	46.0%	18.33	2200
WS-1	6	150	211.6135	111.01	47.5%	15.12	2268
WS-33	3	27	100.2332	90.24	10.0%	31.93	862
WS-32	3	27	99.1741	89.59	9.7%	32.27	871
WS-38	3	27	92.4830	84.42	8.7%	34.60	934
WS-23	3	45	107.3810	81.51	24.1%	29.80	1341
WS-28	3	45	97.8929	74.88	23.5%	32.69	1471
WS-25	3	45	96.9927	70.69	27.1%	32.99	1485
WS-31	3	45	92.2413	69.98	24.1%	34.69	1561
WS-29	3	75	112.1133	67.29	40.0%	28.54	2141
WS-22	3	75	102.6015	59.72	41.8%	31.19	2339
WS-24	3	75	102.3710	59.27	42.1%	31.26	2344
WS-26	3	75	100.8884	60.03	40.5%	31.72	2379
WS-27	3	75	94.3259	54.38	42.3%	33.92	2544
WS-21	3	90	96.7657	52.45	45.8%	33.07	2976

1. WS is label for willow sample. Each number represents a specific sample ID number.

Mechanical Properties

A listing of compressive strength test data is provided in Table 10. The table lists the sample ID, the microwave exposure time, the moisture loss, the diameter and length of each sample, the power density and the recorded compressive strength of each sample as well as the mean and standard deviation (SD) of the three samples tested immediately after exposure and at four, 24 and 48 hrs after exposure. The mean compressive strength results are graphically presented in Figure 9.

Table 9. Relative Xylan Extract Strengths

Sample	Sample Length	Applied Power	¹H NMR peak area	Relative Xylan in Extract
	In	KJ/Kg		
Control		0	469	1
Blank		0	438	0.93
WS-38	3	934	429	0.91
WS-13	6	671	427	0.91
WS-17	6	1054	413	0.88
WS-11	6	1059	410	0.87
WS-6	6	1758	408	0.87
WS-28	3	1470	380	0.81
WS-5	6	1914	380	0.81
WS-25	3	1484	359	0.76
WS-22	3	2339	338	0.72
WS-4	6	1775	335	0.71
WS-1	6	2268	327	0.70
WS-29	3	2140	327	0.70

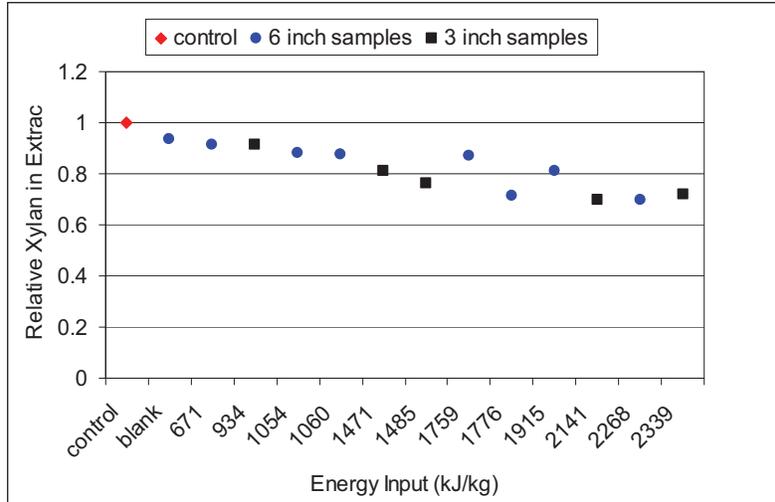


Figure 8. Xylan extracted from microwave treated willow sticks using alkali

The data show that the radiation induced an increase in the strength of the willow samples, which increased approximately 20 percent in the first 24 hours after microwave treatment and returned to the original strength after 48 hours. These data suggest that the rapid heating of the wood and any associated steam release (steam explosion) was insufficient to degrade the wood structurally and that the initial drying and expansion of the samples (sample bloating) increased the wood strength.¹³

¹³ While steam release and steam explosion did occur during processing, the results suggest that the temperature and pressure conditions within the woody mass were insufficient to degrade the wood. Data presented by Li 2010 suggest that internal temperatures of woody cells must reach 168°C to induce bursting of cells. It is unlikely that this temperature was achieved under the processing conditions in the given applicator (see Relevant Microwave Application Literature Section).

Table 10. Compressive Strength Data Table

Sample	Microwave Exposure Time (s)	Moisture Loss (% of Initial wt)	Diameter (mm)	Length (mm)	Power Density Per Initial Wt (kW/kg)	Compressive Strength (psi)	Test Period
W-2	120	40.3%	45.44	151.38	14.35	5831	21-04 10am
W-3	120	41.0%	43.64	153.93	14.07	4842	21-04 10am
W-5	120	42.9%	41.79	152.12	15.20	6705	21-04 10am
Mean		41.4%	43.62	152.48	14.54	5793	
SD		1.4%	2.58	1.31	0.59	932	
W-6	120	41.7%	42.30	152.38	14.97	6112	21-04 2pm
W-7	120	40.5%	42.50	152.87	14.79	5641	21-04 2pm
W-8	120	40.4%	42.70	152.62	14.33	6387	21-04 2pm
Mean		40.9%	42.50	152.62	14.70	6047	
SD		0.7%	0.20	0.25	0.33	377	
W-1	120	40.5%	45.80	152.81	14.03	5712	22-04 10am
W-9	120	40.9%	43.71	153.07	14.74	6695	22-04 10am
W-10	120	42.6%	41.64	152.89	14.65	6877	22-04 10am
WS-10	120	43.5%	40.16	152.29	16.35	6518	22-04 10am
Mean		42.3%	41.84	152.75	15.25	6696	
SD		1.3%	1.78	0.41	0.96	179	
W-4	120	37.5%	44.88	155.85	12.65	4888	23-04 10am
W-11	120	41.4%	43.02	152.15	14.47	6276	23-04 10am
W-12	120	38.9%	43.07	154.9	13.31	5331	23-04 10am
Mean		39.3%	43.66	154.30	13.48	5498	
SD		2.0%	1.06	1.92	0.92	709	

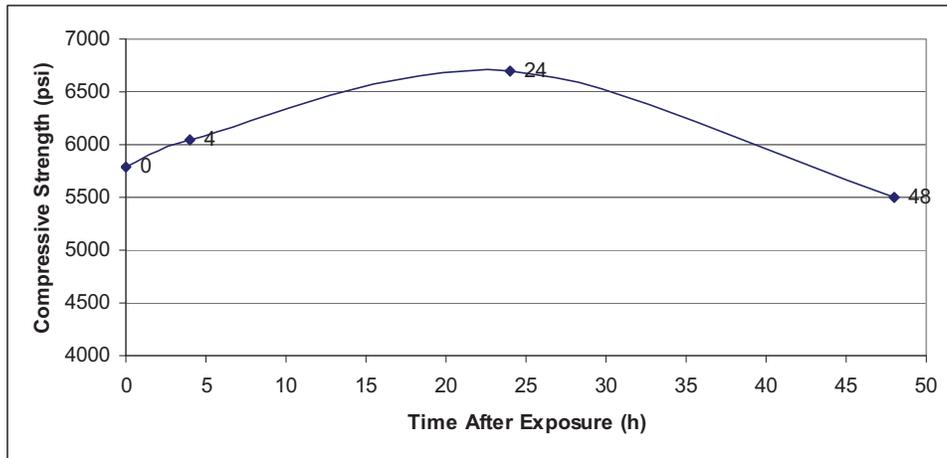


Figure 9. Compressive Strength of Microwave Processed Samples After Exposure

HIGH POWER TESTING

PRIMARY OBJECTIVE

The primary objective of the high power tests was to determine if an increase in microwave power density could induce a more dramatic breakdown in the recalcitrance of woody biomass to hemicellulose extraction and enzymatic hydrolysis than was suggested by the low and medium power test results. The basis for these tests was the premise that a high-applied power density could promote a rapid generation of internal superheated steam in the source material with mini internal “steam explosions” in the porous and cellular structure of the feedstock. It was also assumed that if the internal pressure could not be rapidly dissipated, due to a low surface area to volume ratio (A/V) of the wood sample, then the steam pressure buildup inside the matrix would be more likely to induce structural transformations, when compared to a sample with a high A/V ratio. The test program was designed to examine these issues.

GENERAL APPROACH

Willow and pine feedstock samples with different A/V ratios and maple chips were all prepared and subjected to high-powered microwave application using special microwave applicators ranging in applied power from 15 to 40 kW. Tests were performed at Thermax-Thermatron facilities located in Louisville, Kentucky. The samples were exposed to microwaves at atmosphere pressure.

TEST EQUIPMENT

Two applicators were employed: 1) a 20 kW, 2450 MHz, variable power, resonant cavity applicator, shown in Figure 10, and 2) a 100 kW, 915 MHz, variable power, traveling wave applicator, shown in Figure 11. Feedstock samples were introduced into each respective applicator using a 1¼-inch quartz tube described in detail below.

The 20 kW applicator used was a Thermex TM20S, 20kW 2450 MHz microwave generator connected to a plasma applicator with a quartz tube through the middle. A three-stub tuning device was placed between the generator and the applicator and adjusted to reduce the reflected power. Figure 10 shows two photographs of this resonant cavity applicator. For most samples approximately 10 to 15 kW of power was supplied during sample processing. Samples were introduced into the applicator by means of a 1-¾ inch quartz tube, shown in Figure 10. The left photograph shows the cavity and the quartz tube extending from the cavity. The plasma unit has a diameter of 1¼ inches with a working length of 12-inches. Cut-off tubes on either end were approximately six inches each. The right photograph shows plasma formation induced during processing by excess energy introduced into the reactor.

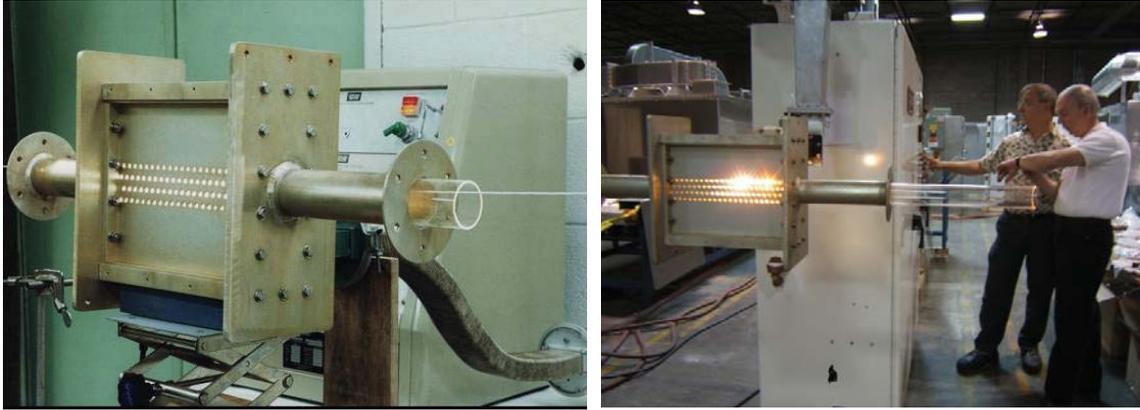


Figure 10. 20 kW Resonant Cavity Applicator

The 100 kW traveling wave applicator used in the testing program was a Thermex TM100, 100kW 915 MHz Microwave Generator outfitted with a traveling wave applicator and a water load to absorb any power not used to heat the material inserted into the traveling wave applicator. **Figure 11** shows two photographs of the traveling wave applicator. For most samples approximately 25 to 40 kW of power was supplied during sample processing. The left photograph shows the U shaped waveguide with a 1- $\frac{3}{4}$ inch quartz tube extending from the sampling port, similar to the 20 kW applicator. The right photograph shows a close up of the quartz tube and a willow stick sample.



Figure 11. 100kW Traveling Wave Applicator

WILLOW FEEDSTOCK TEST FLOW DIAGRAM

Willow sample processing was divided into five steps shown in Figure 12. These steps included:

1. Sample Type,
2. Pretreatment Sample Modification,
3. Microwave Pretreatment,
4. Extraction Sample Modification,
5. Extraction and Hydrolysis Methods.

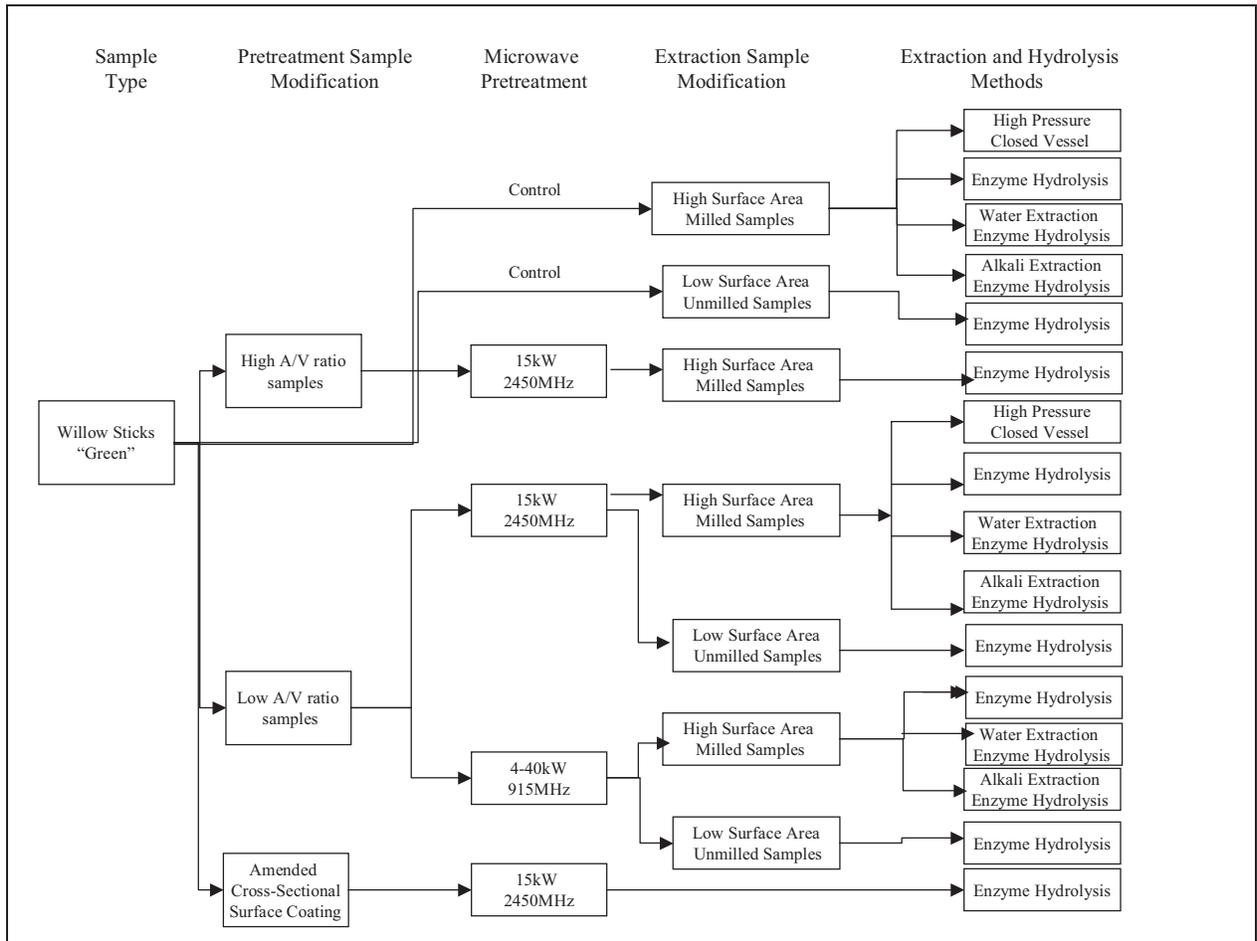


Figure 12: Willow sample high power microwave processing flow diagram

1. Sample type

The willow feedstocks samples used in the willow-testing program were comprised of willow sticks and willow disks. Both sticks and disks were approximately 1½-inch diameter willow branches that were harvested from SUNY ESF plots in Central NY. It was necessary to target 1½-inch diameter branches because the high powered 20 kW and 100 kW Thermex applicators, previously summarized, could not readily process feedstock sizes with greater diameters.¹⁴ The harvested willow branches, bark intact, were cut to two length sizes: 1½ inches and nine inches. The 9-inch size samples were referred to as sticks and the 1½-inch samples were referred to as disks. The prepared samples were frozen while “green” until needed for testing. A photograph of the willow stick and disk samples is shown in Figure 13.

2. Pretreatment Sample Modification

Cutting the harvested branches to different lengths produced test samples with differing cross sectional area to total volume ratios (A/V). This provided a means to process samples with the same volume but different A/V ratios. Processing samples as such meant that power density (expressed in terms of kW per sample volume) could be held constant for the different A/V ratio samples. This was accomplished by placing six, 1½-inch disk samples in the reactor and comparing the results of these samples with that of a 9-inch stick sample. The different A/V ratio samples, characterized as low A/V ratio samples and high A/V ratio samples, are identified under Sample Modification in Figure 12. Three types of samples were used in the willow-testing program: 1) Low A/V ratio sticks, 2) High A/V ratio disks and 3) Surface coated samples.

Low A/V ratio “stick” samples were produced by cutting samples to nine inches in length. By reducing the cross sectional surface and increasing the escape length of moisture from the cross sectional area it was hoped to increase internal pressure and maintain moisture for longer periods within the sample during high powered processing.

High A/V ratio “disks” samples were produced by cutting samples into 1½-inch lengths. The 1½-inch samples were designed to provide shorter escape routes and larger surface areas for the release of the moisture contained within the wood sample, compared to that of the low cross sectional area stick samples. The short moisture escape routes in the 1½-inch long disks were expected to reduce the buildup of pressure in the sample.

¹⁴ The quartz tubes used to introduce the sample into the microwave applicators were 1¾ -inch in diameter. This limited the size (diameter) of the feedstock samples.



Figure 13: Willow sticks and disks ready for microwave treatment

Amended cross sectional surface coating samples refers to specially prepared “stick” samples, the ends of which were heavily coated with Elmer’s wood glue, in an attempt to prevent the release of moisture and induce a greater buildup of internal pressure within the woody structure.

3. Microwave Pretreatment

Microwave pretreatments were performed in the 20 kW, 2450 MHz resonant cavity applicator (described above) at power settings of 15 kW for 10 to 30 seconds, and in the 100 kW, 915 MHz traveling wave applicator (described above) at power levels ranging from 4-to-40 kW, applied for periods ranging from for two to 10 seconds.

4. Extraction Sample Modifications

Prior to extraction, the wood samples were processed to produce high surface area extract samples (milled samples) and low surface area extract samples (nonmilled samples). These samples were prepared to assess whether microwave processing could facilitate the extraction process of low surface area samples, thereby reducing the need for extensive and energy intensive milling. The two sample types were prepared as follows:

High surface area extraction samples were prepared after processing for extraction testing by slicing the samples and milling the center slice to pass through a #30 mesh sieve. Prior to milling, the samples were air dried to aid in the milling process. Air-drying helped to prevent the wood meal from sticking together, which prevents the meal from passing through the screen mesh.

Low surface area extraction samples were prepared after processing by dividing the samples into wedges. Nine-inch (stick) samples were cut to remove three inches from the end and then four slices, $\frac{3}{4}$ -inch thick were sliced from the center of the stick. Wedges were produced by splitting the slices into four wedges in preparation for extraction testing. These samples were not milled.

5. Extraction and Hydrolysis Methods

Three types of extraction techniques were employed during the testing program:

1. High pressure closed vessel extractions,
2. Water extractions,
3. Alkali extractions.

Enzyme hydrolysis was performed on samples extracted with both water and alkali solutions. Additional description of these techniques is presented below:

High pressure closed vessel extractions (hot water extraction) was performed at a 5:1 liquor to wood ratio on milled samples using the Ethos TC microwave digester. Samples were extracted at 140°C for two hrs and analyzed in a method as described previously in the low power testing section. Extracted solids were measure on samples subjected to this extraction method.

Water extractions were performed on milled wood samples, extracted with water at a 5:1 liquor to wood ratio for 24 hours in 50°C oven while being rotated. After the water extraction, the samples were then washed three times with deionized (DI) water prior to enzyme hydrolysis (see below).

Alkali extractions were performed on milled wood samples with a 2.5N NaOH solution at a liquor to wood ratio of 5:1 for 24 hours in 50°C oven while being rotated. After extraction, the samples were washed with DI water to a neutral pH before enzyme hydrolysis.

Enzyme hydrolysis was performed on milled and wedge samples of microwave pretreated willow and untreated willow (control) before and after water and alkali extractions, using a method adapted from the National Renewable Energy Laboratory LAP-009.¹⁵ The glucose that was liberated from the samples was then compared on an oven dry wood basis for the microwave and control samples to assess improvements in extraction due to the pretreatment.

WILLOW TESTING AND RESULTS¹⁶

Willow tests, depicted in the Figure 12 test diagram, and the test results are presented below and include:

¹⁵ In this procedure, 0.25 g of wood meal was added to a 20 ml scintillation vial. Following that, 5ml of 1molar 4.8 pH sodium citrate buffer, 30ul of cycloheximide solution (10 mg cycloheximide/ml in water), 40 ul tetracycline solution (10 mg tetracycline/ml in 70% ethanol), and enough water was added to the scintillation vial to bring the volume to 9.8 ml. The scintillation vial was sealed and placed on a rotator in a 50°C oven for several hours to wet the wood and bring the temperature to equilibrium (NOTE: the tops on the vials may become brittle during the hydrolysis and crack, if checking appears replace the top with a new one). A mixed enzyme solution was made such that 0.2 ml contained cellulase enzyme with FPU=6 and 1mg of β -glucosidase enzyme. 0.2 ml of the solution was then added to the vials at hydrolysis time 0 hrs. At determined intervals 7.5 ul of the solution was withdrawn from the vials and analyzed with a Gluicell glucose meter to find glucose content of the sample.

¹⁶ Note that internal willow wood temperature measurements taken after microwave treatment and microscopic examination of the willow are presented in separate sections in this report.

- Control tests (no microwave pretreatments) – Hot Water¹⁷ Solids Extraction; and Cold Water Extraction¹⁸ with Enzyme Hydrolysis
- High A/V ratio willow disk tests using 15 kW, 2450 MHz power – Cold Water Extraction and Enzyme Hydrolysis
- Low A/V ratio willow stick tests using 15 kW, 2450 MHz and 40 kW, 915 MHz power – Hot Water Solids Extraction and Cold Water Extraction with Enzyme Hydrolysis
- Surface coated willow stick tests using 15 kW, 2450 MHz power – Cold Water Extraction with Enzyme Hydrolysis.

The last two tests were designed to evaluate the effects of milling prior to extraction to see whether microwave treatment could reduce the need for milling. The tests include:

- Cold water (50°C) and alkali (NaOH) extractions of milled willow sticks treated with 15 kW, 2450 MHz and 40 kW, 915 MHz microwave using enzymatic hydrolysis (glucose production) as a measure of microwave effectiveness
- Cold water (50°C) and alkali (NaOH) extractions of non-milled willow sticks treated with 15 kW, 2450 MHz and 40 kW, 915 MHz microwave using enzymatic hydrolysis (glucose production) as a measure of microwave effectiveness.

Solids Extraction Control and Willow Sticks Treated at 15 kW

Initial high power application tests were conducted to determine whether high power could induce excess hemicellulose extraction using solids extraction as an indicator test.¹⁹

Two willow samples (an untreated control sample and a microwave treated sample) were tested to see if willow stick samples subjected to at 15 kW microwave power for 20 seconds could induce a greater solids extraction than an untreated control sample. After treatment, each stick was milled and extracted at 140°C for two hours and the mass loss of each sample was determined. The results showed very little change, and actually suggested a decrease in extractability. The willow control had ~5.5% mass loss while treated sample (WS1520) had ~3.5% mass loss. A loss in sample extractability with microwave treatment was also seen in other feedstock test data as discussed below.

Glucose Production from Control Willow Samples

Glucose production (expressed as % of wood) from the control samples is presented in Table 11. Initial 24 hr production rates averaged 7.6% and final (168 hr) rates reached approximately 12.4%.

¹⁷ Hot water (140°C) extractions

¹⁸ Cold water (50°C) extractions.

¹⁹ To simplify the experimental process, the wood mass loss during extraction was used as an indicator of the mass of hemicellulose extracted. The use of solids loss as an indicator test is based on the assumption that hot water solubility of lignin and cellulose are relatively low, therefore most of the solids lost during the treatment are expected to be hemicellulose. This procedure was also employed during low solids testing.

Table 11. Control Test Willow Data

Sample	Treatment		Mass		Glucose Liberated (% of cellulose in wood)		
	kW	sec.	As Is ¹ (g)	O.D. ² (g)	24hrs	48hrs	168hrs
Control	0	0	0.279	0.253	7.5%	9.9%	12.7%
Control	0	0	0.275	0.249	7.7%	10.2%	12.0%

1. Sample weight after processing.
2. Sample weight after oven drying

Glucose Production of High A/V Willow Samples treated at 15 kW

High A/V microwave treated willow samples (disks), air dried and milled to #30 mesh were subjected to enzyme hydrolysis and the production of glucose measured. The results are tabulated in Table 12. The data presented show that initial 24-hour rates averaged approximately 8.4% glucose, somewhat higher than the controls samples, but final rates after 168 hours were approximately 12.8%, similar to the control samples.

Table 12. High A/V Ratio Willow Data

Sample	Treatment		Mass		Glucose Liberated (% of cellulose in wood)		
	kW	sec.	As Is ¹ (g)	O.D. ² (g)	24hrs	48hrs	168hrs
Disk	15	12	0.293	0.251	8.3%	10.7%	12.7%
Disk	15	12	0.29	0.249	8.4%	10.1%	12.8%

1. Sample weight after processing.
2. Sample weight after oven drying

Glucose Production of Low A/V Willow Samples treated at 15 and 40 kW

Low A/V microwave treated willow samples (sticks), air dried and milled to #30 mesh were subjected to enzyme hydrolysis and the production of glucose measured. The results are tabulated in Table 13. The data presented show that initial 24 hours glucose production ranged from 7.0 to 12.8%, and final 168-hour production ranged from 11.1 to 15.9% exceeding the control and High A/V samples. Power levels (15 or 40 kW) did not substantially alter the observed results.

Table 13. Low A/V Ratio Willow Data

Sample	Treatment		Mass		Glucose Liberated (% of cellulose in wood)		
	kW	sec.	As Is ¹ (g)	O.D. ² (g)	24hrs	48hrs	168hrs
Stick	40	10	0.304	0.248	12.2%	14.0%	15.8%
Stick	40	10	0.3	0.245	10.5%	14.5%	12.8%
Stick	15	30	0.29	0.252	8.2%	10.4%	11.1%
Stick	15	30	0.288	0.250	7.0%	10.4%	11.5%
Stick	15	20	0.32	0.248	12.8%	14.0%	15.9%
Stick	15	20	0.317	0.246	11.9%	14.4%	15.3%

1. Sample weight after processing.
2. Sample weight after oven drying

Glucose Production of Surface Coated Low A/V Willow Samples treated at 15 kW

Microwave treated willow samples (sticks and disks), air dried and milled to #30 mesh were subjected to enzyme hydrolysis and the production of glucose measured. The results are tabulated in Table 14. The data presented show that coating the ends of stick samples with glue did not result in improved glucose production, and results were similar to the control samples.²⁰

Table 14. Surface Coated Willow Data

Sample	Treatment		Mass		Glucose Liberated (% of cellulose in wood)		
	kW	sec.	As Is ¹ (g)	O.D. ² (g)	24hrs	48hrs	168hrs
Glued Stick	15	20	0.305	0.248	8.3%	9.8%	11.2%
Glued Stick	15	20	0.298	0.242	8.3%	9.9%	11.2%

1. Sample weight after processing.
2. Sample weight after oven drying

²⁰ It is possible that the glue coating may have absorbed some of the applied energy reducing the effectiveness of microwave processing.

The data presented in Table 11, Table 12, Table 13, and Table 14 is graphically depicted in **Figure 14**. The results show two levels of glucose production; the higher level being the Low A/V ratio willow stick data, and the lower level being the control, High A/V and surface coated data.

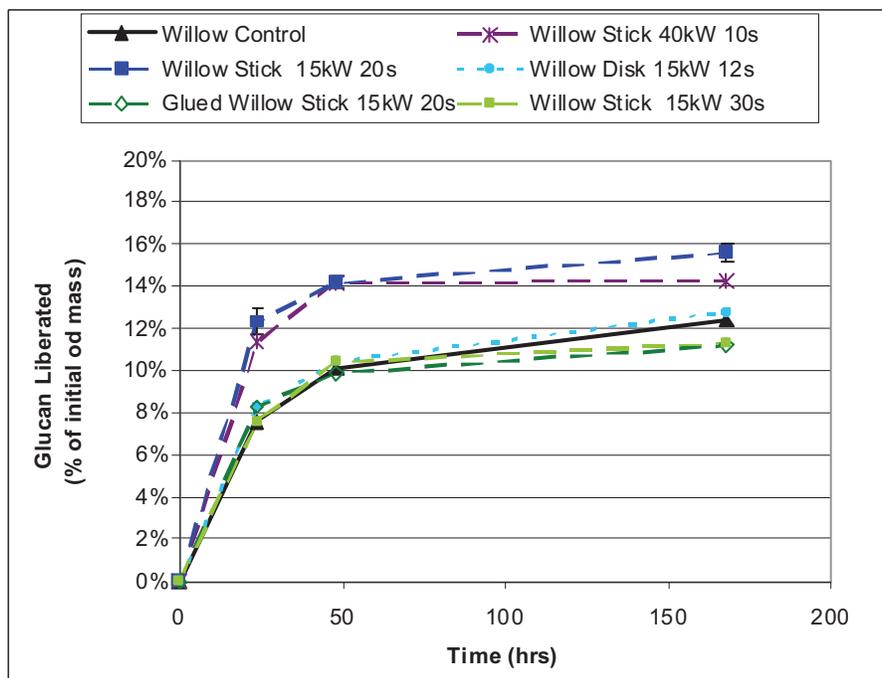


Figure 14: Enzyme hydrolysis of microwave treated willow.

Glucose Production of Treated, Milled Willow with Water and Alkali Extraction

Willow samples that were microwave treated, then milled, were extracted with water or alkali. The results are listed in Table 15 and graphically depicted in Figure 15. The samples that were extracted with alkali showed a larger increase in the production of glucose over the water-extracted samples, though with exception of a few data points. The water extracted control had less cellulose hydrolyzed, 8% as compared to 10%, for the previous control sample, which was most likely due to drying of the samples after the water extraction. Power levels (15 or 40 kW) did not appear to be a significant factor.

Glucose Production of Treated, Non-Milled Willow with Water and Alkali Extraction

Microwave treated willow sticks were cut into wedges then enzyme hydrolyzed. The results are listed in Table 16 and graphically depicted in Figure 16. The amount of glucose that was liberated from the wedges was small in comparison to the amount that was liberated from the milled sample, and there was a lot of variation between samples. This variation was most likely due to variations in microwave treatment within a sample as well as size variation between samples. Power levels (15 or 40 kW) did not appear to be a significant factor.

Table 15. Enzyme hydrolysis of milled willow sticks after cold water and alkali extractions

	Pretreatment		Extraction	Mass ¹ O.D. (g)	Glucose Liberated (% of cellulose in wood)		
	kW	Sec			24hrs	48hrs	120hrs
Control	0	0	Water	0.371	5.1%	7.5%	8.6%
Control	0	0	NaOH	0.266	18.2%	26.9%	32.3%
Stick	40	10	Water	0.278	8.1%	11.1%	10.9%
Stick	40	10	NaOH	0.298	16.5%		
Stick	15	20	Water	0.227	6.3%	11.7%	12.9%
Stick	15	30	Water	0.347	5.6%	8.3%	10.4%
Stick	15	30	NaOH	0.268	17.6%	19.5%	30.3%

1. Sample weight after oven drying

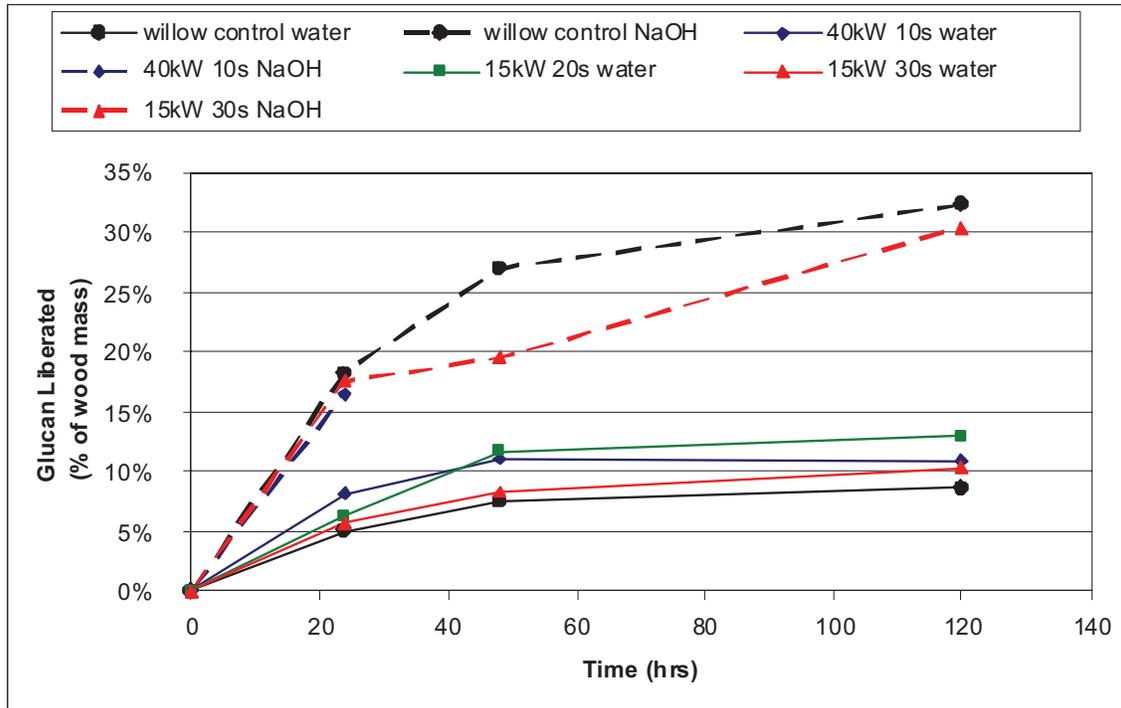


Figure 15: Enzyme hydrolysis of microwave treated willow sticks after alkali or cold water extraction.

Table 16: Enzyme hydrolysis of wedges from microwave treated willow sticks.

Sample	Treatment		Mass as is (g)	O.D. (g)	Glucose Liberated (% of cellulose in wood)				
	kW	sec.			24hrs	48hrs	72hrs	144hrs	192hrs
Control	0	0	23.0	10.4	0.51%	0.68%	0.78%	0.91%	0.99%
Control	0	0	28.2	12.7	0.39%	0.53%	0.61%	0.66%	0.75%
Stick	15	20	25.8	11.6	0.59%	0.85%	1.00%	1.28%	1.25%
Stick	40	5	24.2	10.9	0.53%	0.76%	0.91%	1.13%	1.26%

1. Sample weight after processing.
2. Sample weight after oven drying

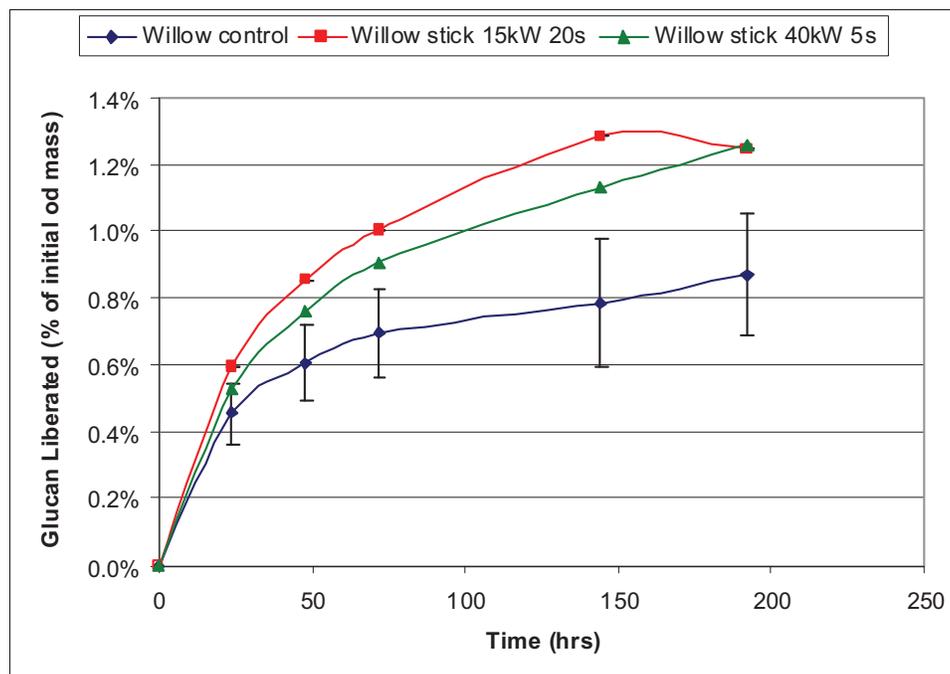


Figure 16. Enzyme hydrolysis of wedges from microwave treated sticks

PINE STICK TEST FLOW DIAGRAM

Pine stick processing was also divided into five steps, as shown in Figure 17. These steps included:

1. Sample Type,
2. Pretreatment Sample Modification,
3. Microwave Pretreatment Moisture,
4. Extraction Sample Modification,
5. Extraction and Hydrolysis Methods.

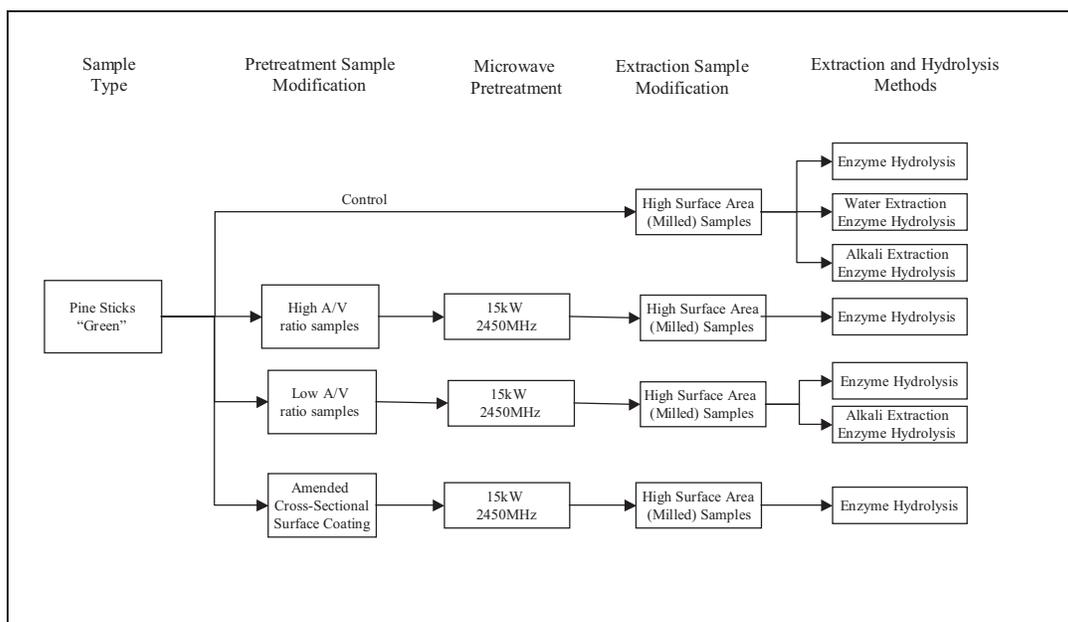


Figure 17. Pine stick high power microwave processing flow diagram.

1. Sample type

The pine feedstock samples used in the high powered pine testing program were white pine sticks cut from limbs and stems with diameters less than 1½ inches.²¹ Only a limited number of the sticks were available to fit into the 1¾ inch diameter quartz tube for microwave treatment, resulting in a limited number of pine tests.

²¹ The quartz tubes used to introduce the sample into the microwave applicators were 1¾ -inch in diameter. This limited the size (diameter) of the feedstock samples.

2. Pretreatment Sample Modification

Low A/V ratio “stick” samples were produced by cutting samples to nine inches in length. As in the willow samples, by reducing the cross sectional surface and increasing the escape length of moisture from the cross sectional area, it was hoped to increase internal pressure and maintain moisture for longer periods within the sample during high-powered processing.

High A/V ratio “disk” samples were produced by cutting samples into 1¹/₂-inch lengths. The 1¹/₂-inch samples were designed to provide shorter escape routes and larger surface areas for the release of the moisture contained within the wood sample, compared to that of the low cross-sectional area stick samples. The easy escape of moisture was expected to reduce the buildup of pressure in the sample.

Amended cross sectional surface coating of samples, as in the willow testing program, refers to specially prepared “stick” samples, the ends of which were heavily coated with Elmer’s wood glue, in an attempt to prevent the release of moisture and induce a greater buildup of internal pressure within the woody structure.

3. Microwave Pretreatment

Microwave pretreatments were performed in the 20 kW, 2450 MHz resonant cavity applicator (described above) at power settings of 15 kW for 10 to 30 seconds.

4. Extraction Sample Modifications

Only high surface area extraction samples were prepared after processing for extraction testing. This was accomplished by slicing the samples and milling the center slice to pass through a #30 mesh screen. Prior to milling, the samples were air dried to aid in the milling process. Air-drying helped to prevent the wood meal from sticking together, which prevents the meal from passing through the screen mesh.

5. Extraction and Hydrolysis Methods

Two types of extraction techniques were employed during the pine-testing program.

1. Water extractions,
2. Alkali extractions.

Enzyme hydrolysis was performed on samples extracted with both water and alkali solutions. Additional description of these techniques is presented below:

Water extractions were performed on milled wood samples, extracted with water at a 5:1 liquor to wood ratio for 24 hours in 50°C oven while being rotated. After the water extraction, the samples were then washed three times with DI water prior to enzyme hydrolysis (see below).

Alkali extractions were performed on milled wood samples with a 2.5N NaOH solution at a liquor to wood ratio of 5:1 for 24 hours in 50°C oven while being rotated. After extraction, the samples were washed with DI water to a neutral pH before enzyme hydrolysis.

Enzyme hydrolysis was performed on milled and wedge samples of microwave pretreated willow and untreated willow (control) before and after water and alkali extractions, using the aforementioned method adapted from the National Renewable Energy Laboratory LAP-009 (see Willow Testing Extraction and Hydrolysis Methods).

PINE TESTING AND RESULTS

Pine test results, included in the Figure 17 flow diagram, and test results are presented below and include:

- Control tests (no microwave pretreatments) – Cold Water Extraction²² and Enzyme Hydrolysis
- High A/V ratio pine disk tests using 15 kW, 2450 MHz power – Cold Water Extraction and Enzyme Hydrolysis
- Low A/V ratio pine stick tests using 15 kW, 2450 MHz – Cold Water Extraction with Enzyme Hydrolysis
- Surface coated willow stick tests using 15 kW, 2450 MHz power – Cold Water Extraction with Enzyme Hydrolysis
- Selected pine samples treated with 15 kW, 2450 MHz power, subjected to enzyme hydrolysis after water and alkali extractions
- Control (untreated samples) subjected to enzyme hydrolysis after water and alkali extractions.

Enzyme Hydrolysis of Microwave Treated Pine Samples

Pine sticks that were microwave treated, then milled, showed lower rated of enzyme hydrolysis than those that were not microwave treated (see Figure 18). The pine sticks that were used were of a diameter less than one inch as these sticks were the only size that were long enough and still able to fit in the quartz. After treatment, the sticks appeared dry and showed some scorching. The drying of the sticks likely resulted in a collapse of pore structure and decreased availability of enzyme active sites.

Enzyme Hydrolysis of Microwave Treated, Milled, then Alkali Extracted Pine Wood.

Treatment of the pine stick with NaOH increased the 48 hr hydrolysis of the control sample from 4.7% to 8.5% glucose liberated and increased the 48 hr hydrolysis of the microwave treated samples from 1.5% to 4% glucose liberated. In all cases the cellulose hydrolysis was greater for the control pine samples most likely due to the drying that occurred in the microwave treated samples.

Glucose Production from Control Pine Samples

Glucose production (expressed as % of wood) from the control samples is presented in Table 17. Initial 24 hr production rates averaged approximately 4.0% and final (168 hr) rates reached an average of 4.8%.

²² Cold water (50°C) extractions.

Table 17. Control Test Pine Data

Sample	Treatment		Mass		Glucose Liberated (% of cellulose in wood)		
	kW	sec.	As Is ¹ (g)	O.D. ² (g)	24hrs	48hrs	168hrs
Control	0	0	0.294	0.254	3.6%	3.7%	4.9%
Control	0	0	0.287	0.248	4.3%	5.6%	4.7%
1. Sample weight after processing. 2. Sample weight after oven drying							

Glucose Production of High A/V Pine Samples Treated at 15 kW

High A/V microwave treated pine samples (disks), air dried and milled to #30 mesh were subjected to enzyme hydrolysis and the production of glucose measured. The results are tabulated in Table 18. The data presented show that glucose production rates were significantly lower than the control samples, reaching a maximum yield of 2.4% after 168 hrs, compared to 4.8% for the control (untreated samples). After treatment, the sticks appeared dry and showed some scorching. The drying of the sticks may have actually resulted in a collapse of pore structure and decreased availability of enzyme active sites.

Table 18. High A/V Ratio Pine Data

Sample	Treatment		Mass		Glucose Liberated (% of cellulose in wood)		
	kW	sec.	As Is ¹ (g)	O.D. ² (g)	24hrs	48hrs	168hrs
Disk	15	20	0.298	0.255	1.7%	1.9%	2.4%
Disk	15	20	0.291	0.249		1.8%	
1. Sample weight after processing. 2. Sample weight after oven drying							

Glucose Production of Low A/V Pine Samples Treated at 15 kW

Low A/V microwave treated pine samples (sticks), air dried and milled to #30 mesh were also subjected to enzyme hydrolysis and the production of glucose measured. The results are tabulated in Table 19. The data is similar to the High A/V samples and show poor glucose production rates, significantly lower than the control samples. This was also attributed to excessive moisture loss and drying of the sticks that may have resulted in a collapse of pore structure and decreased availability of enzyme active sites.

Table 19. Low A/V Ratio Pine Data

Sample	Treatment		Mass		Glucose Liberated (% of cellulose in wood)		
	kW	sec.	As Is ¹ (g)	O.D. ² (g)	24hrs	48hrs	168hrs
Stick	15	20	0.295	0.252	1.3%	1.5%	
Stick	15	20	0.294	0.251	1.2%	1.3%	1.5%

1. Sample weight after processing.
2. Sample weight after oven drying

Glucose Production of Surface Coated Low A/V Pine Samples Treated at 15 kW

Surface coated pine samples (sticks), air dried and milled to #30 mesh were subjected to enzyme hydrolysis, and the production of glucose measured. The results, tabulated in Table 20 show that treated coated stick samples did not result in improved glucose production and exhibited lower yields than the control samples.

Table 20. Surface Pine Coated Data

Sample	Treatment		Mass		Glucose Liberated (% of cellulose in wood)		
	kW	sec.	As Is ¹ (g)	O.D. ² (g)	24hrs	48hrs	168hrs
Glued	15	20	0.282	0.246			
Glued	15	20	0.284	0.248		1.1%	1.2%

1. Sample weight after processing.
2. Sample weight after oven drying

The data presented in Table 17, Table 18, Table 19, and Table 20 are graphically depicted in Figure 18. The results show two levels of glucose production. The higher level is the pine control samples. The lower level depicts the microwave treated samples, all of which yielded significantly lower glucose than the control samples.

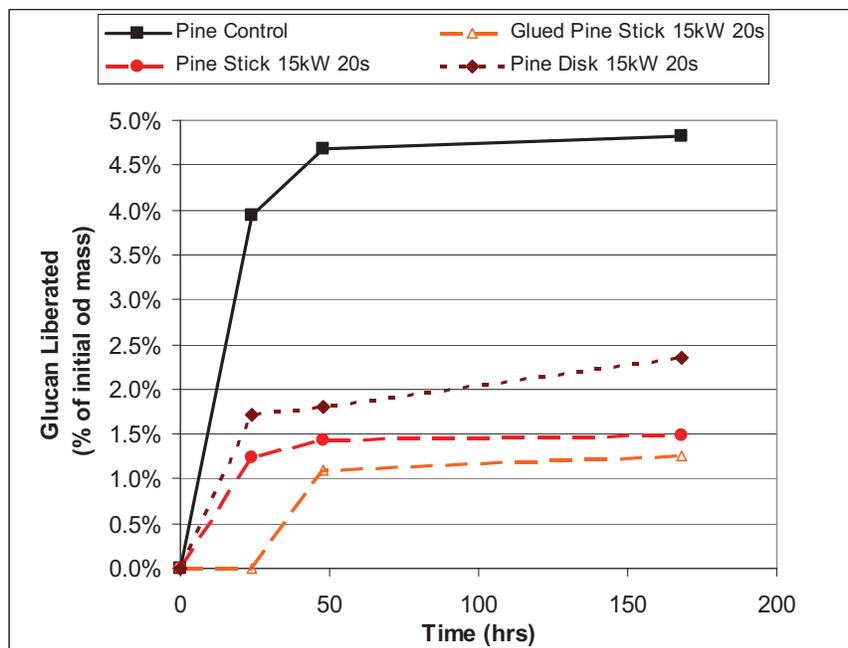


Figure 18. Enzyme hydrolysis of white pine after microwave treatment

Glucose Production of Treated, Milled Pine with Water and Alkali Extractions

Glucose production in both the control and microwave treated pine samples were compared to determine whether alkali (NaOH) extractions might result in more aggressive yield in the microwave treated samples when compared to cold-water extractions. The results are presented in Table 21 and graphically depicted in Figure 19. Treatment of the low A/V pine stick with alkali (NaOH) increased the glucose yield when compared to the cold-water extraction by a factor between two and three times. Alkali extraction resulted in higher yield values for the treated microwave samples when compared to the water extraction data (see Table 19). In all cases, however, the cellulose hydrolysis (glucose production) was greater for the control pine samples, most likely due to the drying that occurred in the microwave treated samples.

Table 21. Enzyme hydrolysis of pine wood microwave treated and caustic extraction

	Pretreatment		Extraction	Mass O.D ¹ . (g)	Glucose Liberated (% of cellulose in wood)		
	kW	Sec			24hrs	48hrs	120hrs
Control	0	0	Water	0.241	2.8%	3.1%	3.3%
Control	0	0	NaOH	0.195	7.3%	8.6%	10.5%
Low A/V Sample	15	20	NaOH	0.249	2.8%	3.9%	4.5%

1. Sample weight after oven drying

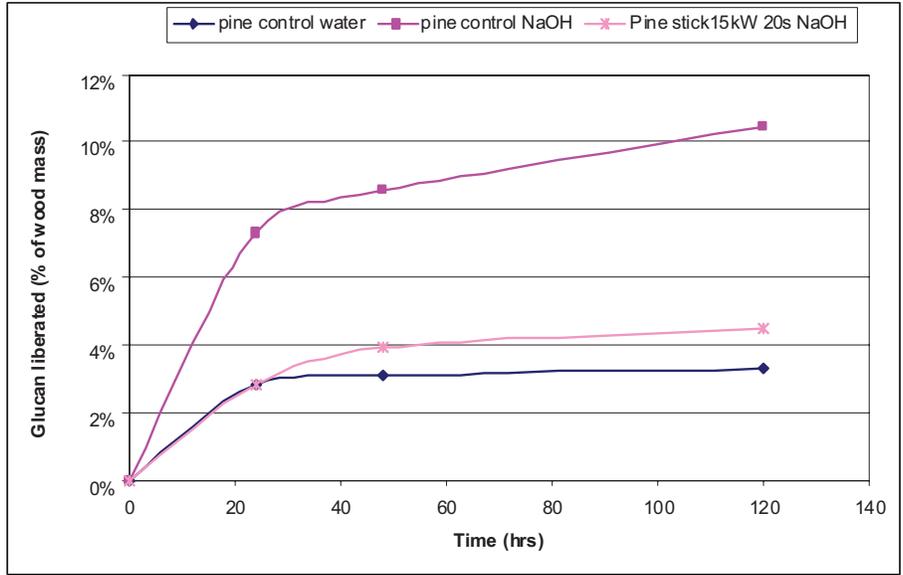


Figure 19: Enzyme hydrolysis of microwave treated white pine after alkali extraction.

MAPLE WOOD CHIP TEST FLOW DIAGRAM

Maple wood chip processing was divided into four steps as shown in Figure 20. These include:

1. Sample Type,
2. Microwave Pretreatment Moisture,
3. Extraction Sample Modification,
4. Extraction and Hydrolysis Methods.

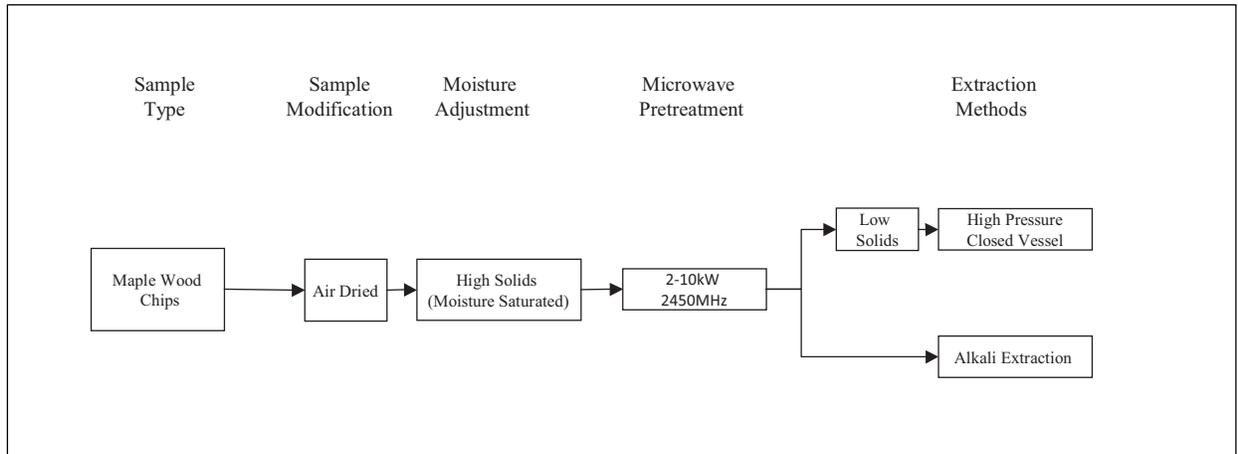


Figure 20. Maple wood chip high power microwave processing diagram

1. Sample type

Sugar maple logs 4-ft long with diameters ranging from 4-to-10 inches were debarked, chipped, screened to pass 1¹/₄ inch diameter screen and be retained on ⁵/₈ inch diameter screen, and air dried for storage at the SUNY ESF department of paper and bioprocess engineering laboratory.

2. Moisture Modification

The moisture content of the chips was modified prior to treatment to yield a moisture-saturated sample (approximately 50% moisture). The sample was produced by soaking the air-dried chips in deionized (DI) water for 24 hrs. After the soaking time, the chips were then placed on a screen and allowed to drain for 15 minutes to remove excess water.

3. Microwave Pretreatment

Microwave pretreatment (Thermex TM20S, 20kW 2450 MHz Applicator) was performed on water saturated sugar maple chips at power levels ranging from 2-to-10 kW, 2450 MHz for periods ranging from 3-to-24 seconds. Each sample's approximate oven dry mass was 31g. This quantity of saturated maple wood chips was contained within a 6-inch length of the 1³/₄-inch inner diameter of the quartz tube that was inserted into the 20 kW applicator (based on an average of 10 loadings). Samples were loaded into the quartz tube and centered in the application area of the resonant cavity applicator.

4. Extraction Methods

High pressure closed vessel (hot water extraction) was performed at a 5:1 liquor to wood ratio on microwave treated maple chips using the Ethos TC microwave digester. Samples were extracted at 140°C for two hours and analyzed as described previously in the low power testing section.

Alkali extractions were used to extract hemicellulose from maple wood chips. Chips were extracted with 4M NaOH for 24 hrs at a 5:1 liquor to wood ratio. The extract was then separated from the chips and the chips washed with water until neutral. The extract was neutralized with acetic acid, and then precipitated with 10 parts ethanol and further washed with ethanol to remove residual salts. The precipitant was then oven dried at 60°C to determine the residual mass of extract.

MAPLE WOOD CHIP TESTING AND RESULTS

The mass solids extraction results of both the hot water and alkali extraction tests after microwave pretreatment at power ranging from 2-to-10 kW and frequency exposure levels at 2450 MHz are presented in Table 22. The results are reported as mass loss in percent of original dry mass for the hot water and alkali extractions. The total mass loss reported for the alkali extracts includes hemicelluloses that precipitated in an additional ethanol washing step. Results are presented below.

Hot water extraction

The extract of microwave treated wood chips (extracted with hot water at 140°C for two hours). remained nearly clear with little mass loss. The data was highly variable, suggesting slight mass gains or slight mass losses from treated samples with no apparent pattern. These data, shown in Table 22, suggest that the treatment provides no measurable effect on the maple chips.

Alkaline extraction

The alkaline extraction with 4M NaOH was more effective on the control samples than on the treated samples. The data in Table 22 show that both the total mass loss and the ethanol precipitate loss was greater in the control samples (total mass loss of 14.7% and precipitate [hemicellulose] loss of 4.0%) than any of the treated samples. These data suggest that the treatment provides no measurable effect on the maple chips.

Table 22. Hot water and alkali extraction of high power microwave treated wood chips.

Sample #	Microwave treatment		Hot Water	4M NaOH Extraction	
			Mass Loss	Total Mass Loss	Ethanol Precipitate
	Time (sec)	Power (kW)	(% mass)	(% mass)	(% mass)
Control	0	0		14.7%	4.0%
14	3	2	-0.3%		2.4%
15	6	2	0.5%		2.8%
16	12	2	-0.5%		2.0%
17	24	2	-0.3%		2.9%
18	3	4	-0.6%		2.9%
19	6	4	1.4%		1.7%
20	12	4	-1.0%		1.1%
21	24	4	-2.3%		1.3%
22	3	8	-0.8%	11.9%	2.4%
23	6	8	1.7%	12.7%	1.5%
24	12	8	-0.1%	11.4%	2.2%
25	24	8	-2.5%	8.9%	2.1%
26	3	10	0.7%		2.4%
27	6	10	-4.1%		2.2%
28	10	10	0.7%		2.8%

WILLOW SAMPLE TEMPERATURE MEASUREMENTS

Objective

Internal willow stick and disk internal temperature measurements were taken to determine whether the internal steam induced by high powered microwave applicators could reach superheated steam temperatures that might facilitate a breakdown in the lignocellulosic structure of the treated samples.

General Approach

A 1/16" pilot hole was drilled into the test material, immediately after processing (within 30 seconds), and a J-type thermocouple was inserted into the hole and the temperature was recorded.

Test Equipment

A Fluke 52II Thermometer was used to measure the internal temperature.

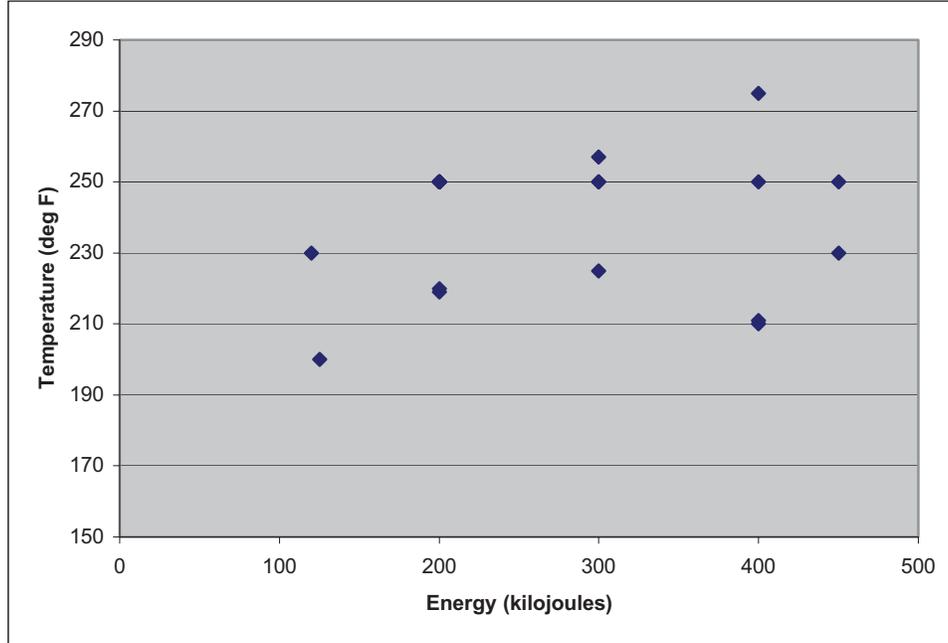
Temperature Results

The results reported in Table 23 show that internal temperature ranged between a low of 210°F (98.9°C) and a high of 275°F (135°C). Most of the samples, regardless of the applied energy, exhibited slightly superheated internal temperatures. This is shown in the scatter plot presented in **Figure 21**.

Table 23. Internal applied energy and temperature data

Sample ID	Green sample wt(g)	Freq	Power	Time	Energy	Temp
		(MHz)	(kW)	(sec)	(kJ)	(deg F)
W7	203.78	915	15	8	120	230
W8	244.02	915	25	8	200	250
W9	194.57	915	25	8	200	250
W11	210.11	915	25	5	125	200
W12	201.24	915	25	12	300	225
W13	194.87	915	25	12	300	250
W14	207.71	915	40	5	200	220
W15	246.14	915	40	5	200	250
W16	162.33	915	40	5	200	250
W18	179.20	915	40	5	200	250
W19	224.25	915	40	10	400	275
W20	250.84	915	40	10	400	250
W21	217.54	2450	15	20	300	257
W25	227.72	2450	15	30	450	230
W26	255.37	915	40	5	200	250
W27	239.35	915	40	5	200	219
W28	254.56	915	40	10	400	211
W29	263.30	915	40	10	400	210
*W32	262.93	2450	15	20	300	250
*W33	186.32	2450	15	30	450	250
* GLUE ON ENDS						

Figure 21. Energy-Temperature Data



WILLOW STICK MICROSCOPIC EXAMINATION

Objective

A microscopic examination of willow sticks exposed to 40 kW of microwave energy for five seconds and 15 kW for 30 seconds was undertaken to determine whether a breakdown in the cellular structure of the woody matrix could be observed. Physical evidence or the lack of physical evidence of a structural breakdown could provide a physical basis for the increase (or decrease) in alkali-induced extractables.

General Approach

Samples of willow sticks were cut into slices then cleaned with a razor blade for a clean picture surface, and placed under a Nikon Optiphot optical microscope for analysis. Magnification was approximately 10:1. Photographs were taken of the samples to record the observations.

Examination Results

Light microscopy images (see below) gave some evidence of macro level changes to the wood. These changes can be observed by comparing the control willow (no microwave exposure), presented in Figure 22 to microwave treated samples presented in Figure 23, Figure 24, and Figure 25.

The observed radial and tangential cracking of the willow stick was attributed to the rapid buildup of steam-induced pressure within the stick due to the fast rate of microwave heating within the samples and the low rate of steam and water diffusion from the sample. These pressures were able to overcome the failure strength of the samples at weak porous locations in the woody matrix, resulting in cracks radiating outward from the center and tangential to the

wood at the outer layers. Some of the cracks, especially those in the radial direction, may be a result of fast and unequal drying of the samples; similar cracks are often seen in poorly cured lumber. This explanation is not as likely for the tangential cracks.

These “macro-cracks” were not visually judged to be of sufficient magnitude to measurably impact the sample in a manner that would reduce the recalcitrance of the sample (e.g., enhance subsequent extraction and hydrolysis of the sample). It is believed that a “micro-scale” disruption of the woody structure would be required to affect the recalcitrance of the biomass. Nonetheless, such treatment could reduce the physical strength of the sample, assuming that the loss of moisture during microwave treatment could be controlled.²³

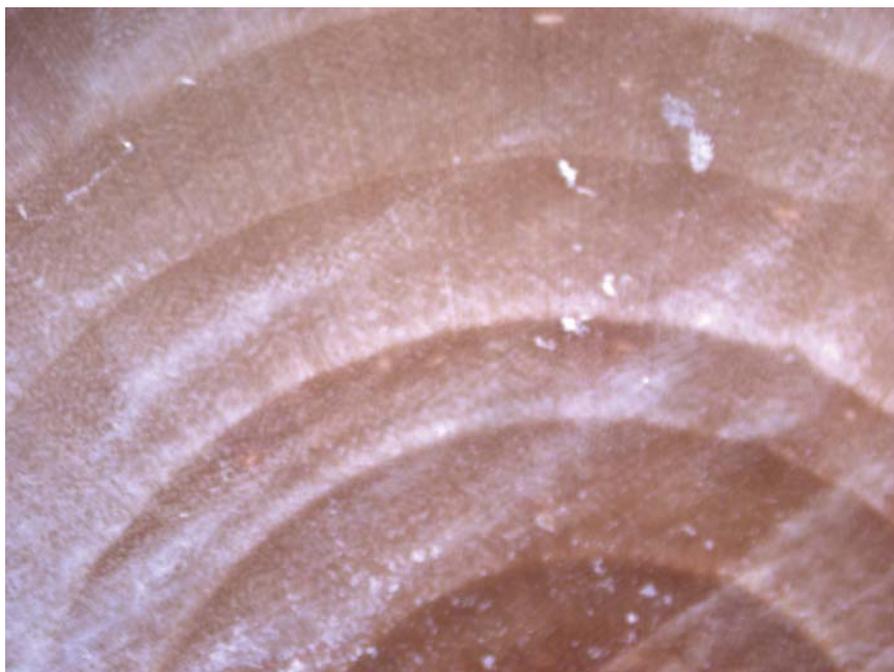


Figure 22: Control (no microwave treatment) willow sample

²³ A reduction in wood strength could reduce milling requirements resulting in energy savings during processing, however, as shown in the previous Medium Power Testing section, increases in wood strength accompanied wood drying, even with macro-scale deformation of the willow samples.

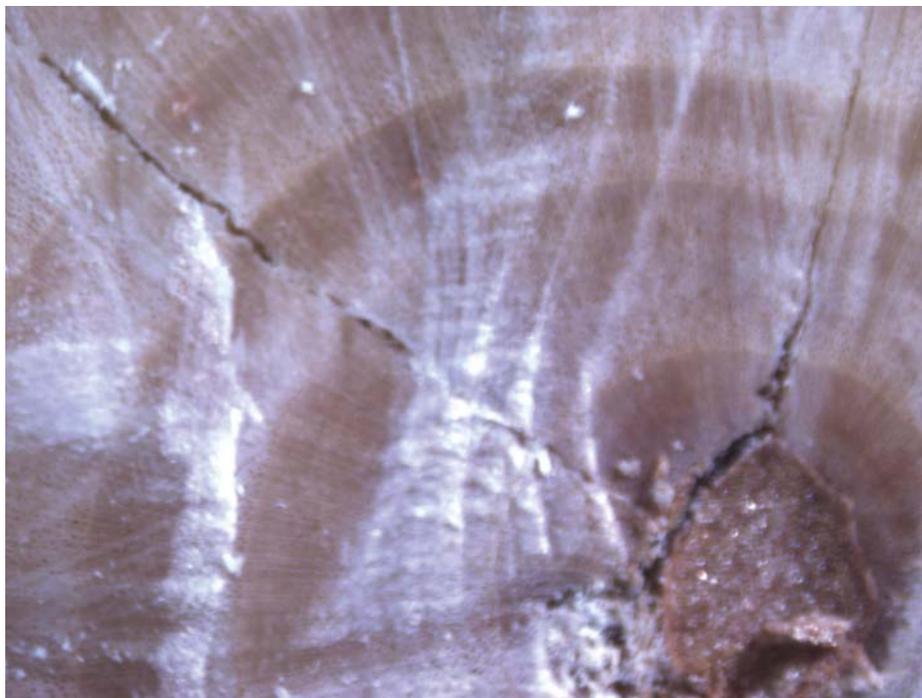


Figure 23: Cracks radiating from center of willow stick after treatment at 40kW for 5 seconds.

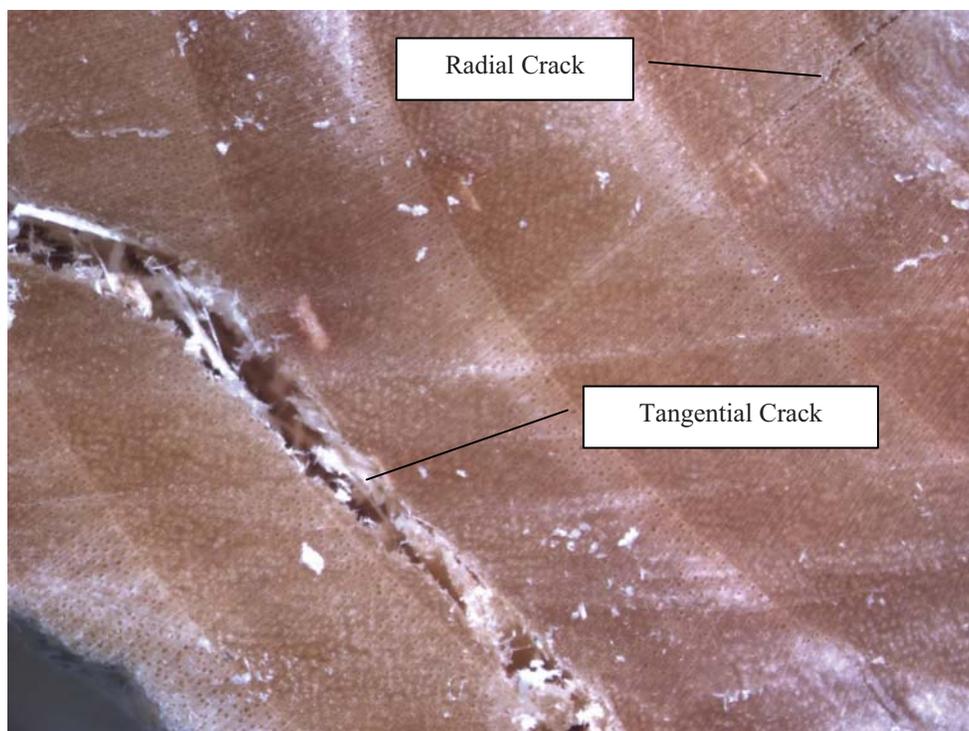


Figure 24: Radial and tangential cracks induced in willow through microwave treatment at 40kW for 10 seconds.



Figure 25: Radial cracks in willow stick microwave treated at 15kW for 30 seconds.

FINDINGS, CONCLUSIONS AND RECOMMENDATIONS

FINDINGS

The following is an outline summary of the findings of the **low power** testing effort:

- Under atmospheric pressure conditions where feedstock temperatures of only +/- 100°C could be achieved, maple chip mass breakdown was not significant
- Where temperatures above 140°C could be achieved, in pressurized reactors, maple chip mass breakdown in low solids conditions was measurable
- Amendment addition of acetic acid was found to be effective in improving woody mass breakdown, but only at elevated pressures and corresponding temperatures
- High solids processing (moisture contents between seven and 50%) did not provide any measurable benefit over low solids (80% moisture content) in pressurized reactors
- In non- pressurized reactors the samples dried rapidly, and charred if moisture was not maintained in the sample feedstock
- Observed microwave benefits could only be attributed to temperature effects. No special radiation effects were observed.

The following is an outline summary of the findings of the **medium power** testing effort:

- Medium power microwave application (3.2 KW) applied under atmospheric conditions did not affect the woody feedstock structure or enhance extraction sufficiently to be used as a substitute for more aggressive alkali extraction methods
- Medium power microwave treatment did generate sufficient internal steam pressures to disrupt the macro-scale structure of the treated wood, however, such breakdown did not affect the internal cellular structure of the wood matrix sufficiently to reduce recalcitrance above that which might be anticipated by any other hot water treatment
- Excessive microwave exposure will dry the biomass resulting in an increase in wood strength and not the desired decrease.

The following is an outline summary of the findings of the **high power** testing effort:

High power microwave application at atmospheric pressure generated moderate superheated temperatures within the woody sticks (willow and pine) tested.

- A rapid release of moisture and drying of the wood was associated with all high power microwave tests

- High power microwave treatment did generate sufficient internal steam pressures in the willow and pine feedstocks to disrupt the macro-scale structure of the treated wood
- Glucose production (enzymatic hydrolysis) was reduced in willow and pine biomass, subjected to high power microwave application, and this was attributed to the drying of the wood and possibly the collapse of the pore structure of the biomass.

CONCLUSIONS

It was concluded from the investigation that:

- Microwave processing of biomass offers no special advantage over conventional heat processing
- To achieve measurable benefits, solution temperatures must approach 200°C, requiring the use of pressurized reactors
- The maintenance of adequate moisture in biomass feedstock or processing in a solution is the only practical way to employ microwave in biomass pretreatment
- While high- powered microwave radiation can induce steam explosions inside the biomass structure and disrupt the macro-scale structure of the biomass, such explosions accompanied by the rapid loss of moisture and wood drying tend to increase the recalcitrance of the biomass, thereby reducing enzymatic hydrolysis yields.

RECOMMENDATIONS

It is recommended that future work on microwave applicators focus on their potential use in high- pressure microwave applicators and the development of systems where sufficient moisture can be maintained during processing. A rapid increase in temperature without drying of the biomass could potentially induce macro-structural changes due to internal steam explosions, and rapid buildup of superheated temperature conditions could induce micro-cellular changes that might enhance hemicellulose extraction and enzymatic hydrolysis.

Though this strategy increases the complexity of the application system, pressure and temperature conditions at atmospheric pressure were found to be insufficient to induce measurable biomass breakdown.

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