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Mechanical Property Evaluation of Torrefied Biomass Materials with Correlation to Grinding Efficiency

Xin Zhou
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Mechanical Property Evaluation of Torrefied Biomass Materials with Correlation to Grinding Efficiency

Xin Zhou

Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of

**Master of Science
in
Mechanical Engineering**

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**Department of Mechanical and Aerospace Engineering
Morgantown, West Virginia
2011**

Keywords: biomass, torrefaction, hybrid work index, hardness, elastic modulus

Abstract

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Xin Zhou

Motivated by the transition to a more sustainable society, biomass, currently the largest renewable energy source in the world, could therefore in principle become a key energy source in the future. Co-combustion of these materials and coal can lead to a significant reduction in carbon dioxide net emissions in new and existing power plants while potentially reducing capture costs as well. However, many challenges remain to be solved before biomass can be used on a much larger scale as a sustainable energy source. Some of these challenges are related to biomass production, land management, and competition with food production; but challenges also exist in the handling of biomass as a fuel. The relatively low-energy density of biomass, in combination with its high moisture content, makes transport of biomass from production sites to power stations or future bio-refineries costly. Due to this reason, torrefaction is required, where in the raw biomass is thermally treated in the absence of oxygen at relatively low temperature ranging from 200-300°C. This mild treatment both increases the energy density and facilitates grindability by weakening the fibrous structure and tenacity of biomass. During the process the biomass also decreases in mass, but will maintain the majority of its initial energy.

Historically, the Hardgrove Grindability Index (HGI) has been used to assess fuel grinding energy, and yet this parameter is incapable of categorizing raw or torrefied biomass materials. The objective of this research is to conduct material mechanical property evaluation of torrefied biomass and identify the correlation related to grindability as well as grinding energy assessment.

This work involves the influence of torrefaction temperature and residence time, flow rate of inert gas, size reduction via ball-milling (energy consumption for grinding), and mechanical property evaluation (hardness, elastic modulus, fracture toughness). Torrefaction leads to a very substantial improvement of the grindability. It therefore provides a solution to the problems concerned with biomass gasification and co-firing with coal where size reduction of biomass materials is required.

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Chapter 1: Introduction

1.1 Problem Statement

The attenuation of carbon dioxide (CO_2) levels in the atmosphere has been an important ecological issue associated with global warming. As Figure 1 illustrates, the concentration of CO_2 is four times higher than it was 100 years ago due to consumption of fossil fuels. In view of the worldwide concern about the depletion of fossil fuels and environmental problems associated with the use of these sources, renewable energy sources are receiving increased attention [4]. Biomass is currently the largest source of renewable energy in the United States as shown in Figure 3. It has several advantages compared to other renewable sources. First, biomass is a widely available and untapped source of energy until recently. Second, solar conversion equipment and fuel cell cost much more than biomass. The specific cost is given in Figure 4. Third, the coal fed power generation stations can easily integrate into the biomass conversion facility. Fourth, although there is a debate on burning biofuels which also releases carbon dioxide, a nearly equivalent amount of carbon dioxide is captured through photosynthesis during growth of biomass. The growth of plants and their conversion of solar energy to biomass fuels recycle atmospheric carbon. As a result, Sustainable cultivation and harvesting of biomass can result in no net increase in CO_2 emissions as illustrated in Figure 2. The low sulfur content of most biomass materials means that emissions of sulfur dioxide gas are minimized. Moreover, the emission of nitrogen oxides is also decreased as demonstrated in Figure 5. Gasification technologies play a key role in expanding the use of biomass as a major renewable energy source. [11] Advantages of torrefaction as a pretreatment prior to gasification are demonstrated. The overall exergetic efficiency of air-blown gasification of torrefied wood was found to be lower than that of wood, because the volatiles produced in the torrefaction step are not utilized. For the entrained flow gasifier, the volatiles can be introduced into the hot product gas stream as a 'chemical quench'. The overall efficiency of

such a process scheme is comparable to direct gasification of wood, but more energy is conserved in as chemical energy in the product gas (72.6% versus 68.6%). This novel method to improve the efficiency of biomass gasification is promising. [5]

Figure 1: Greenhouse Gas Concentration in History [40]

Figure 2: Carbon Dioxide Recycle by Using biofuels

Figure 3: U.S. Energy Production in 2009 [41]

Figure 4: U.S. Energy Cost in 2009 [41]

Figure 5: NO_x Reduction from Biomass/Coal Co-Firing [42]

Co-firing is one of the simplest ways of utilizing biomass to displace fossil fuels which requires no new investment or specialized technology. It refers to blending biomass with coal in conventional boiler to generate power. Many electric utilities in the United States have successfully experimented co-firing with additional low cost less than 0.5 cents/KWh compared to coal firing alone. However, size reduction of biomass materials is the major problem in co-firing. Size of biomass materials must be reduced to less than several hundred microns for complete combustion. Yet the biomass size reduction can be difficult and expensive due to the fibrous structure that is not easy to break down. Torrefaction is a thermal treatment at a temperature of 200-300°C near atmospheric pressure in the absence of oxygen. This thermal treatment destroys the fibrous structure of biomass in order to reduce grinding energy consumption. Furthermore, torrefaction decreases the mass of raw biomass and maintains most of its initial energy in the solid product. This increase of the calorific value is important for overall energy conversion efficiency.

1.2 Research Objective

There are three objectives in this research. First, design and construct an effective torrefaction system for biomass materials to improve grindability of biomass. Decomposition mechanism during the biomass torrefaction process and related parametric studies such as Influence of torrefaction temperature, time and flow rate of inert gas on grindability of biomass will be studied as well. Second, establish a Hybrid Work Index (HWI) for grinding of torrefied biomass materials from combination of Resistance of Impact Milling and Bond Work Index. The HWI could potentially become a standard for size reduction of biomass materials. Third, mechanical properties of torrefied biomass materials will be evaluated for correlation to grinding efficiency.

There are three main chapters in this thesis. Chapter 2 provides an introduction of torrefaction process and decomposition mechanism of biomass. Entrained gas-flow torrefaction system is applied to produce torrefied biomass materials. There is a cover for each experimental unit's function and combination of all units. Some basic knowledge about cell structure of biomass will be discussed for better understanding of the decomposition mechanism of biomass.

Chapter 3 mainly discusses about Hybrid Work Index. Ball-milling method is also applied for grinding biomass materials. Size reduction and energy consuming of biomass materials with different torrefied temperature and time will be evaluated to establish their relation.

Chapter 4 is about mechanical property evaluation of torrefied biomass materials. Hardness, Young's Modulus and Fracture Toughness values of biomass materials will be acquired to determine their relation to grinding efficiency. The relation between mechanical property and decomposition mechanism is discussed.

Finally, results and conclusion are presented in Chapter 5 and Chapter 6.

Chapter 2: Torrefaction of Biomass

2.1 Torrefaction Background

Wood has been used as a fuel for thousands of years. Raw wood has too much moisture content (~50%). When wood is burned, incomplete combustion occurs with the formation of smoke, carbon monoxide and many volatile organic compounds (VOCs). Biomass torrefaction technology, as a promising way to improve fuel properties, was developed in the 1980's by Pechiney, a French company, to commercially convert wood into torrefied wood. They used torrefied wood as a replacement of charcoal to produce metals from metal oxides. This heat treatment process uses inert gas to drive out the moisture, gases and VOCs. [36] Over the last 30 years, several technologies have been developed to improve the torrefaction process by using high pressure steam [5], high temperature inert gas [8] and superheated steam [13].

Torrefaction provides biofuels that are rich in energy, low in moisture content, resistant to decay and easily pulverized or densified [6]. By integrating production of higher value bioproducts into biofuel and power output, overall profitability and productivity of all energy related products are potentially improved [7].

2.2 Cell Structure of Biomass

There are three main sugar-based polymeric structures of biomass: cellulose, hemicellulose and lignin. These structures are found in cell walls of plants, which provide the mechanical strength and toughness for biomass. Different compositions of polymeric structures are found in various biomass materials, displayed in Table 1.

Table 1: Composition of Different Biomass [1]

Biomass	Lignin	Cellulose	Hemicellulose
Willow	25%	50%	19%
Larch	35%	26%	27%
Straw	14.2%	34%	27.2%
Beech	11.6-22.7%	33.7-46.4%	17.8-25.5%

A typical cell structure of a plant is illustrated in Figure 6. Where it shows cellulose is the main structure of cell walls; hemicellulose is the binding matrix between each cellulose fiber and lignin is the mutual coherence of different cell walls. Figure 7 shows the composition of cellulose, hemicellulose and lignin in wood.

Figure 6: Detailed Impression of the Structure of a Cell Wall. (a) part of the cell wall and middle lamella, primary wall and secondary cell wall, (b) macrofibril mutual structure, (c) microfibril structure, (d) individual cellulose polymers including micelles, and (e) mutual coherence of individual cellulose polymers on a micro level [20]

Figure 7: Wood Microscopic Structure [9]

2.3 Decomposition Mechanisms during Torrefaction

There are three decomposition mechanisms in biomass which are (1) hemicellulose decomposition, (2) cellulose depolymerisation, and (3) lignin degradation. Upon torrefaction (200°C-300°C), mass loss is predominantly from the decomposition of hemicellulose and some of lignin [1], especially, hemicellulose decomposition has its peaking rate of decomposition between 250°C to 280°C. Depending on biomass species, typically, cellulose depolymerisation of biomass is not prevalent in the temperature range of 200°C-300°C. Figure 8 shows thermogravimetry of cotton wood whereas between 200°C and 300°C, the xylan-based hemicellulose has high rate of decomposition and the cellulose has very little depolymerisation (i.e. mass loss). Among these three decomposition mechanisms, hemicellulose decomposition is the most reactive polymer and is assumed to be the main cause of the change of mechanical property after biomass torrefaction. Up to 250°C, cellulose depolymerisation does not involve serious mass loss and the effect of lignin decomposition is small, e.g. Figure 8. After torrefaction, biomass becomes brittle, hydrophobic (<3% moisture content) and loses about 30 percent of its mass while retaining 90 percent of its original energy content (9,500 to 11,000 Btu/lb, comparable to coal), The corresponding strength loss of mechanical property is due to hemicellulose decomposition. Specifically, for typical untreated biomass materials, the highly structured cellulose fibers are oriented and interlinked with hemicellulose matrix. However, during the biomass torrefaction process, destruction of the hemicellulose matrix is no longer capable to support the highly structured cellulose fibers. Therefore, the cellulose fibers are loosed such that they are easily detachable and breakable. Thus, compared to untreated biomass materials, torrefied biomass materials are more brittle and have lower mechanical properties. Furthermore, less grinding energy is needed for size reduction and smaller, more spherical particles can be produced.

Figure 8: Thermogravimetry of Cotton Wood [21]. (The green lines are the torrefaction temperature range)

2.4 Torrefaction Process Definition

Biomass torrefaction is a heat treatment process to improve thermal properties of raw biomass materials. Torrefied biomass retains most of its chemical energy and is resistant to moisture and decay. Moreover, it becomes brittle and can be grinded easily. When biomass is heated to 160°C, it loses water and retains its physical and mechanical properties. As the temperature rises up to between 180°C and 280°C, moisture, carbon dioxide, large amounts of acetic acid and low weight VOCs are removed, producing a hydrophobic solid product with an increased energy density (on a mass basis) and greatly increased grindability [14–18]. In general, energy consumption for size reduction of torrefied wood is 50–85% smaller in comparison with fresh wood [1,19]. When biomass is exposed to above 280°C, it starts to be gasified and transform into combustible gases including methane, carbon monoxide, hydrogen and tars which reduces the energy density of biomass [36].

2.4.1 Mass and Energy Yield

Torrefaction decreases the O/C ratio, the quantity of syngas produced increases with the severity of the torrefaction [8]. Organic material of biomass

contains all of its chemical energy and after torrefaction, most of its energy is left in the torrefied product. Table 2 demonstrates ratio of carbon increases and ratio of oxygen decreases after torrefaction.

Table 2: Composition of Wood and Torrefied Wood (for Willow) [5]

Material	Raw Willow	Torrefied Willow (250°C, 30min)	Torrefied Willow (300°C, 10min)
Carbon	47.2%	51.3%	55.8%
Hydrogen	6.1%	5.9%	5.6%
Oxygen	45.1%	40.9%	36.2%
Nitrogen	0.3%	0.4%	0.5%
Ash	1.3%	1.5%	1.9%
LHV(MJ/kg)	17.6	19.4	21.0

A two-step reaction in series model is found to give an accurate description, as shown in Figure 9. The first reaction step has a high solid yield (70–88 wt%, decreasing with temperature), whereas less mass is conserved in the second step (41 wt%). The fast initial step may be representative for hemicelluloses decomposition, whereas the slower subsequent reaction represents cellulose depolymerisation and secondary charring of hemicelluloses fragments) [10].

Figure 9: Two-Step Mechanism with Parallel Reactions for Formation of Solids and Volatiles [10]

2.4.2 Torrefaction Temperature and Torrefaction Time

There are several stages during thermal treatment of biomass. First is the heating stage when the temperature is less than 100°C. Around 100°C is the drying stage in which moisture is removed from biomass. Then, between 100-200°C is the intermediate heating stage. Torrefaction only occurs between 200-300°C illustrated by the green horizontal line in Figure 10. After torrefaction, it is the cooling stage of biomass thermal treatment.

Figure 10: Stages of Biomass during Thermal Treatment (green lines mark the torrefaction temperature range) [1]

2.5 Torrefaction Facilities

The thermal pre-treatment of biomass is executed by an entrained gas-flow torrefaction system illustrated in Figure 11. The three main parts of the system are: gas bottle, pre-heater and tube chamber.

The nitrogen gas bottle is attached to a gas regulator using 1/4inch stainless steel tube. The regulator connects to a dryer with a pre-heater, three-way valve and the tube chamber in behind. The moisture is absorbed by TiO_2 particles in the dryer and the nitrogen (N_2) is pre-heated by thermal pad wrapped around the pre-heater. After N_2 is heated up to the desired temperature, it flows through the main chamber. Another thermal pad is applied on the tube chamber to maintain gas temperature. There is a pressure gauge which measures the inside pressure of the chamber in case it builds up too high. A 1 psi check valve near the exit port could release the gas out for safety concerns. The flow rate could be adjusted by a valve in front of the pre-heater. The thermocouple and the

thermal pad are controlled by a controller that is already in the NRCCE High Bay Floor Area.

All thermocouples align with line as flow-through sensors. Temperature could be detected when N_2 passes by. Considering the safety issue, Insulation materials are around the chamber and pre-heater which can also reduce heat loss. There is an exit port in the three-way valve for high temperature N_2 to release out. This port goes straight up to the hood fan. Another exit port is attached to a one-way valve which also connects to the hood fan.

Figure 11: Entrained Gas-Flow Torrefaction System

2.5.1 Thermocouple

A thermocouple is a sensor for measuring temperature. It consists of two dissimilar metals, joined together at one end. When the junction of the two metals is heated or cooled, the resistivity changes result in producing a voltage that can be correlated back to the temperature.

2.5.2 Thermal Pad

Thermal pad consists of foam-like material. It could heat up the temperature to several hundred degrees Celsius, even one thousand degrees Celsius. It is flexible and be able to wrap around any tube or cylinder.

Chapter 3: Size Reduction of Biomass

3.1 Ball Milling of Biomass

Historically, Hardgrove Grindability Index is utilized for grinding of coal particles; nevertheless, it is not proper for biomass materials. Many methods have been investigated to evaluate grindability of biomass materials; however, quantitative evaluation is still lacking to describe their performance. Resistance to impact milling (RIM) can be used as grindability measurement, yet this method requires uniform size and homogeneous character which is not practical for large-scale milling [37]. It is necessary to develop a grinding test which is representative of the entire distribution. Bond Work Index (BWI) has been proved to correlate energy consumption to size reduction of materials. It takes a distribution of large particles and reduces to a defined size via similar recycles of oversized materials. In this paper, by combining RIM and BWI, a Hybrid Work Index (HWI) grindability test procedure is proposed for torrefied biomass materials.

A ball milling instrument is applied to do the grinding of biomass. This ball milling instrument (Figure 12) can grind the biomass into small particles so that it could co-firing with coal particles. There are four stainless steel jars in the ball milling instrument, so four tests could be run simultaneously. A certain amount of stainless steel spheres (Two spheres in 19.5mm diameter, two spheres in 10.0mm diameter and four spheres in 6.0mm diameter) is in the jar for reducing the size of biomass. The rotation speed is set at 300rpm.

Figure 12: MTI Ball-Milling Test Instrument with Four Stainless Steel Jars (From MTI Website)

3.2 Bond Work Index

To develop a grinding work index suitable for biomass materials, we start with a general function of comminution, which gives the relation of the energy, E , needed as particles become smaller.

$$dE = \frac{-c \times dx}{x^n} \quad (1)$$

The most recognized comminution law is Bond's law with $n=1.5$ [38]. After integration, the function becomes:

$$\Delta E = 2c \times \left(\frac{1}{\sqrt{x_2}} - \frac{1}{\sqrt{x_1}} \right) \quad (2)$$

Here, c is a constant related to material, x_2 is feed size and x_1 is product size. Bond used 80% undersize materials passing as his characteristic distribution size. The function would simplify to:

$$W = 10W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) \quad (3)$$

Where W_i represents the energy required to reduce a material from infinite size to 100 microns, indirect measurement could achieve the right value of W_i [39].

3.3 Test Procedure of Ball Milling

A standard test method required to be developed for applying an index of the order of comminution, n , to torrefied biomass material. All the test procedure is introduced by Dr. Dirk Van Essendelft.

1. Sample Preparation

Since the original sample is not uniform and has different shape, it needs to be reduced to a uniform, characteristic size distribution. The Bico Disk Mill could do it with setting a certain width of disk separation distance and it won't allow any large size materials to pass through. Besides, the disk separation distance is controllable.

- 1) Starting with a disk separation distance of 3mm, a sieve machine is used to pick all the sizes smaller than 3.35mm. For the large size materials, it will be repute into and run through Bico Disk Mill. After doing the same procedure several times, most of the sample would pass the defined size.
- 2) Mix the sample together and divide the entire sample into smaller lots via riffle. All lots needs to split into approximately 100ml in volume.
- 3) Put 8 sub samples in the Tap Density Tester and check the standard deviation. Make sure the deviation is smaller than 2%, otherwise, it needs to be remixed and split again.
- 4) After verifying the density, calculate the mass needed to fill 15% volume of the mill pots which is recorded as m_s .
- 5) Weight 16 m_s samples and split into 16 equal fractions through riffle. The deviation of each fraction should not be more than 1%.

2. Pre-test Grinding Curve

A pre-test grinding curve requires to be constructed for each material with certain cut size. The test includes grinding for a certain time, sieving at defined size and repeat these steps.

- 1) Put one prepared m_s sample and fill it into one of the mill pots

- 2) Put certain different size of stainless steel spheres into the mill pot.
- 3) Run the ball mill for a short time and record time as t_i .
- 4) Take the sample out and sieve it at a desired cut size.
- 5) Record the mass of the passing material as m_s .
- 6) Put everything back into the mill pot and run the ball milling for another time t_{i+1} .
- 7) Resieve the sample at the same cut size and record the undersize material as m_{s+1} .
- 8) Repeat step 6) and 7) until 50% of the material passing the desired cut size
- 9) Plot m_i vs. $\sum t_i$ and do the curve fitting
- 10) Find the time that needed to grind to receive 25% material passing from the curve. Record this time as t_s .

3. Grindability Testing

There are 4 mill pots for the ball milling machine, so 4 parallel tests could be run at the same time to achieve the equilibrium condition.

- 1) Take 3 prepared m_s samples to QICPIC to get the starting particle size distribution (PSD).
- 2) Generate 32 $1/4m_s$ sub samples from 8 m_s samples through riffle. Check the weight every time after doing the riffle.
- 3) Take 4 prepared m_s samples and put them into 4 mill pots.
- 4) Put the same amount of stainless steel spheres into each mill pot as in pre-test for grinding curve.
- 5) Grind all samples for time t_s .
- 6) Discharge each mill pot and sieve the samples at the same cut size in Step 2. It should give us 25% undersize material for each pot.
- 7) Mass the oversize material and subtract from m_s , this is the amount needed to feed into the pot, m_t . If $m_t > 1/4m_s$, or if m_t is within 5% of $1/4m_s$, skip step 8) and use $1/4m_s$ as fresh feed.
- 8) Take 4 $1/4m_s$ samples to riffle until the mass is under m_t for each pot.

- a. Set a small riffle with two empty catch basins, b_1 and b_2 .
 - b. Measure the empty container on a balance and subtract it for getting the mass of the sample.
 - c. Take a $1/4m_s$ sample and pour it into the riffle, so there are b_1 and b_2 .
 - d. If the mass of b_1 is below m_t , add b_1 into the container. Otherwise, put b_1 aside.
 - e. Pour b_2 into the riffle.
 - f. Repeat c, d and e until the mass in the container is within 5% of m_t . Record the final mass.
- 9) Reput the oversize material and fresh feed from step 7) and 8) and do the ball milling for time t_s .
 - 10) Resieve the material in each pot at the same cut size.
 - 11) Remass the oversize material and subtract it from original m_s . This would be the target m_t for makeup value.
 - 12) Repeat step 7) and 8) to recharge back to m_s .
 - 13) Calculate the average percentage of undersize material as X_n from all four pots and find t_n through grinding curve gained in pre-test. Introduce an iteration for grinding time as

$$t_{i+1} = \frac{\ln 25}{\ln X_n} (t_i - t_n) + t_s, (i \geq 1), t_{i=0} = t_{i=1} = t_s. \quad (4)$$

- 14) Recharge the oversize and fresh feed to mill pots.
- 15) Grind them for t_{i+1} time.
- 16) Discharge them and sieve at same cut size.
- 17) Repeat step 7) to 16) several times and record grind time and mass of undersize material for each pot of each iteration.
- 18) Calculate the mean and standard deviation of grinding time and undersize mass of each iteration. Equilibrium is assumed to be achieved when last three data points are within 90% of each other.
- 19) Run the undersize material through QICPIC to gain a product PSD.

20) Introduce Hybrid Work Index based on the equilibrium time using similar equations as Bond's.

3.4 Energy Consumption and Size Reduction

Energy consumption is the most concern for grinding of biomass materials. Low cost of grinding brings much benefit during the process of power generation from biomass. Thus, the relation of energy consumption and size reduction is the key of co-combustion of biomass with coal. Due to decomposition of hemicellulose during torrefaction, torrefied biomass materials require much less energy on grinding to the same size than raw biomass materials. However, different torrefaction condition changes the grindability of biomass materials. According to previous tests, biomass materials treated in high torrefaction temperature need less energy in grinding compared to be treated in low temperature. Since high temperature requires more energy, the proper torrefaction temperature obliges to be found for different biomass materials in order to meet the low cost. With the ball milling instrument mention above, grinding energy is able to calculate out and the size distribution of the particles could be acquired by QICPICTM. The biomass sample is taken out periodically from the stainless steel jar to obtain the relation between energy consumption and size reduction. Most of raw biomass particles after grinding are needle-shaped while after torrefaction the particles become sphere due to decomposition of hemicellulose. The binding inside the biomass is not strong enough to hold the fiber together.

Chapter 4: Mechanical Property Evaluation of Biomass

Due to decomposition of hemicellulose, strong binding between celluloses no longer exists. Materials become more brittle after torrefaction. Thus, mechanical property varies compared to raw biomass. Moreover, a relation maybe exists between mechanical property and grinding efficiency.

4.1 Vickers Hardness Measurement

Vickers hardness measurements are made with a low-load hardness tester at load levels ranging from 10 to 1000gr and at a constant indenter dwell time of 15s. All indentation tests are carried under the ambient laboratory conditions. After indentation, the length of each of the two diagonals of the square-shaped Vickers indentation is immediately measured by optical microscopy with two magnifications of 10 and 40 [22].

Figure 13: Vickers Hardness Measurement Vickers Indenter: $A_C(d) = \frac{d^2}{2}$; $\beta = [(180 - 2\alpha)/2]$
 $= 22^\circ$; and $d = 2a$

As shown in Figure 13, the Vickers hardness value can be determined by the average diagonal length, d , estimated from such parameters:

$$H_v = \frac{P}{A_{\text{vic ker s}}} \quad (4)$$

$$A_{\text{vic ker s}} = \frac{d^2}{2 \cos 22^\circ} = \frac{d^2}{2 \sin \frac{136^\circ}{2}} = \frac{d^2}{1.854368} \quad (5)$$

4.1.1 Sample Preparation

Due to the rough surface of biomass, all the samples need to be polished before any test. Sandpapers (Grit 320, 600, 1200) could make the sample surface smooth enough for micro indentation to acquire mechanical property, such as hardness, elastic modulus and fracture toughness. Usually, the sample surface is polished combining with water cooling. However, for biomass sample, water could be absorbed resulting in change of mechanical properties. Figure 14 are biomass samples after polishing for indentation test.

Figure 14: Biomass Sample Preparation for Mechanical Property Evaluation

4.2 Indentation

Indentation is a method often used to find mechanical property of materials. Normally it is non-destructive. The indenter is made of a relatively hard, specific geometrical material in order to hit into the test material with a given load for a certain time. The mechanical property will be gained from the reaction of the test material which is the remaining size and the depth of the indentation left in the test material. The indentation depth and area are able to be measured by various techniques, including depth sensing technology and optical methods. Indentation testing, first developed for steel and other alloys, was quickly found to be useful for ceramics, glass production and so on. It has been used for hardness testing since 1800's, but recently this technique has gone far beyond the capability of original testing procedure and application.

Instrumented Indentation was first developed to determine the material property. It becomes primary testing methods as the new material getting smaller; especially the development of nanotechnology has led the indentation to a high level. The mechanics of instrumented indentation are similar to that of hardness tests where in a rigid indenter is purposely forced into the surface of an unknown material using a specific load. However, instrumented indentation monitors the indentation size and depth during the indentation procedure by using high resolution sensors that are different from the hardness testing which the information is collected only after the test is completed [32].

4.2.1 Spherical Indentation

Hertz became interested in finding the relation of local deformation and pressure between two spherical surfaces while studying the phenomenon of Newton's ring. A relation is represented as a quadratic function.

Stresses and deflections arise from the contact between two elastic solids during indentation testing. The most famous one is the contact between a rigid sphere and a flat surface in Figure 15:

Figure 15: Spherical Indentation

Discovered by Hertz, the radius of the contact circle is related to the applied load, indenter radius, and test material elastic modulus [23]. Equation (6) provides the relation between contact area and indenter material properties where P is the indenter load.

$$a^3 = \frac{3}{4} \frac{PR}{E_R} \quad (6)$$

E_R represents combination of elastic modulus of indenter and specimen. It is also called as reduced modulus given by Equation (7) [24].

$$\frac{1}{E_R} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (7)$$

Pharr and Oliver made an assumption to relate the contact area to indentation depth as Equation (8) [25]:

$$a = \sqrt{hR} \quad (8)$$

It is simplified to Equation (9) [27]:

$$P = (4/3)E_R R^{1/2} h^{3/2} \quad (9)$$

4.2.2 Instrumented Indentation

Instrumented indentation is known for providing elastic modulus and hardness information from the test material. Typically, load and depth information are recorded during the test. With an incremental predefined load and indirect measurement of contact area, test material's modulus and hardness can be calculated.

4.2.2.1 Single Point Unloading

Single point unloading utilizes only one slope within the load displacement curve from which the reduced modulus is calculated, shown in Figure 16. The majority of instrumented indentation systems applying this method provide an accurate measurement of testing materials elastic response. However, this technique requires shallow penetration depth.

Figure 16: Single Point Unloading Curve

The initial unloading slope for a spherical indenter shown in Figure 16 is given by Equation (10) which h is the elastic response displacement, E_R is reduced modulus and R is the radius of the indenter [28].

$$\frac{dP}{dh} = 2E_R R^{1/2} h^{1/2} \quad (10)$$

Equation (11) gives the formula of contact area which a is the radius of contact area.

$$A = \pi a^2 \quad (11)$$

With the Equation (11) and assumption of Equation (8), Equation (12) can be derived.

$$E_R = \frac{1}{2} \frac{dP}{dh} \sqrt{\frac{\pi}{A}} \quad (12)$$

4.2.2.2 Multiple Partial Unloading

Figure 17: Multiple Partial Unloading

The instrumented indentation analysis in the lab employs a variation of the multiple partial unloading techniques. This procedure does not require optical contact area measurement. Observed in Equation (9), throughout a single point unloading indentation, the contact area is needed to calculate the reduced modulus. By knowing the geometry of the indenter, the contact area may then be calculated based on the indentation depth. To determine this depth, very expensive and high precision depth sensors are typically needed. A multiple partial unloading technique on the other hand alleviates this requirement through the use of several unloading points.

Equation (13) is formed because the total deflection h_T is the combination of indentation depth h plus the deflection of loading frame h_s .

$$h_T = h + h_s \quad (13)$$

A derivation of Equation (13) with respect to applied load P forms Equation (14), where dh_s/dP is system compliance which assumed to be constant during the indentation test.

$$\frac{dh_T}{dP} = \frac{dh}{dP} + \frac{dh_s}{dP} \quad (14)$$

By plugging Equation (12) to Equation (14), Equation (15) is formed.

$$\frac{dh_T}{dP} = \frac{1}{2E_R} \sqrt{\frac{\pi}{A}} + \frac{dh_s}{dP} \quad (15)$$

Given the assumption that system compliance remains constant during an indentation test, Equation (16) could be created from Equation (15) with variation on contact area, where i denotes the unloading step number.

$$\left. \frac{dh_T}{dP} \right|_i = \frac{\sqrt{\pi}}{2} \frac{1}{E^* \sqrt{A_i}} + \frac{dh_s}{dP} \quad (16)$$

A comparison and subtraction of two adjacent partial unloadings yields Equation (17), where system compliance cancels out [29].

$$E_R = \frac{1}{2} \sqrt{\pi} \left(\left. \frac{1}{\sqrt{A}} \right|_2 - \left. \frac{1}{\sqrt{A}} \right|_1 \right) \left(\left. \frac{dh_T}{dP} \right|_2 - \left. \frac{dh_T}{dP} \right|_1 \right)^{-1} \quad (17)$$

Solving Equation (9) by deriving with respect to the applied load, dh/dP is found, shown in Equation (18), where the constants R and E_R are the indenter radius and reduced modulus.

$$\frac{dh}{dP} = \left[6R(E_R)^2 \right]^{1/3} P^{-1/3} \quad (18)$$

By substitution, a relationship between the total and system deflections with respect to the load, radius, and reduced modulus are created.

$$\frac{dh_T}{dP} = \left[6R(E_R)^2 \right]^{1/3} P^{-1/3} + \frac{dh_s}{dP} \quad (19)$$

The system compliance is assumed to remain constant throughout the indentation process. Due to this assumption, it can be seen that dh_T/dP and $P^{-1/3}$ have a linear relationship in the form of $y = mx + b$. With the slope m in

Equation (20), the reduced modulus can be calculated, and so does test material's elastic modulus [30].

$$E_R = \sqrt{\frac{1}{6R(m)^3}} \quad (20)$$

4.2.3 Instrumented Indentation System

Although the system design and setup are very simple, it requires considerable amounts of indentation system work experience to carry out a correct test procedure. Due to the high precision of hardware, it is very sensitive to vibration and tampering. As a result, implementing an optical table is necessary to ensure a test steady platform. Besides, drastic temperature change would affect the indentation test because of thermal expansion effects. Figure 18 is the picture of the current indentation system. It requires an actuator, load cell, indenter and certain type of loading frame. Loading frame is to create boundary conditions for starting an indentation test. Actuator could provide the displacement in the scale of nanometers to force the indenter to penetrate into the test material. Load cell is able to collect material's load response which leads to elastic modulus combined with known displacement.

Figure 18: Instrumented Indentation System (Designed by Dr. Jared Tannenbaum)

4.2.3.1 Load Cell

Load cell converts load response to electric signal which can be collected by DAQ (data acquisition board). Load cell deforms when load is applied, which cause the strain gauge to deform. The strain gauge inside the load cell determines the accuracy of load cell. Although the voltage drop across the load

cell is very tiny, it varies when load is applied. A Wheatstone bridge is used to amplify the subtle voltage change which is proportional to the applied load voltage [31].

4.2.3.2 Actuator

A piezoelectric actuator has high displacement resolution. The actuator displacement is a function of applied electric field strength due to piezoceramics. Mechanical strain is created caused by applied electric field. This effect is similar to thermal expansion, yet it is a much faster reaction. The active part of the positioning element, the piezoceramics, consists of a stack of disks separated by thin metallic electrodes [31]. The piezoceramics exhibits a strong stiffness at high pressure which provides stability during the indentation test. It is necessary and important because the system compliance is required to be kept at a minimum. However, factors, such as thermal drift and overheating, need to be considered when using the piezoelectric actuator. It may cause errors and jeopardize the precision.

4.2.3.3 Indenter

The choice of indenter is very important and should be made based on the test material. The indenter must be attached to the indenter holder firmly to minimize the system compliance. Mostly, there are two kinds of indenter: sharp indenter and sphere indenter. Sharp indenter induce more plasticity during the contact and it may be more desirable for thin film which the hardness and modulus are independent of the substrate. On the other hand, sphere indenter gives a transition from elastic to elastic-plastic. Indenter material should have a high elastic modulus, such as sapphire and tungsten. Although Diamond is very hard and transparent, it is very brittle and fragile. [31]

4.2.3.4 Loading Frame

The Loading frame should be constructed heavily in order to minimize the effect of system compliance during the indentation test. Usually made of steel,

the loading frame needs to be well designed and constructed. It must be adjusted to accommodate specimens of various sizes and geometries. Yet the whole system needs to act like a solid throughout the indentation test. Thus, a very rigid stabilizing or clamping element must be used [32]. Weight and size of the system are considered as well. The current loading frame is only considered for lab use only; portability is still an issue when testing an immobile specimen.

4.2.4 Factors Affecting Instrumented Indentation

Although simple in theory, many errors occur during the indentation test due to environmental changes and instrumentation malfunction [31]. Besides, lots of material related issues affect the test result too. Most of these errors are unpredictable yet need to be considered to minimize. Among all these errors, system compliance is the most important factor. Experience shows it affects the slope of the fitted line at low applied loads.

Instrumentation indentation analysis is always assumed stress free for test sample before indentation. In fact, residual stress can be generated from specimen processing and surface preparation. There are many ways to determine this residual stress, such as examining the shape of pile up occurred at the edge of indentation and analyzing the load displacement curve. However, experiments have shown these effects to be too small to measure directly.

4.2.4.1 Surface Roughness

Surface roughness of the specimen could cause errors in determining the contact area between the indenter and specimen due to being measured indirectly from depth of penetration [31]. Surface roughness is characterized by the asperity height and spatial distribution across the specimen surface, this value is quantified by a roughness parameter. Where, the parameter is equal to the maximum asperity height, the indenter radius, and the contact radius obtained under the same load, for a smooth specimen. The overall effect of surface roughness is the reduction of mean contact pressure, thereby increasing the calculated contact radius.

4.2.4.2 System Compliance

System compliance is the deflection of the indentation system during test which is proportional to the applied load [31]. Large applied load would result in large deflection. Large system compliance would make the indentation shallow. The result would come from the response of the system, not the surface of the specimen. Experience shows that the errors in the data caused by this, significantly affect the slope of the fitted line at low applied loads, thus, discarding the initial test data would be more accurate for results.

4.3 Fracture Toughness Measurement

Transparent indenter measurement (TIM) in Figure 19 is developed for material mechanical property evaluation with the use of transparent sapphire Vickers indenter. Light comes through an optical fiber from a light source to the infinite in-line system. It travels through the microscope into an indenter holder where there is a right angle mirror which is able to reflect the light straight onto the sample surface. With refractive matching fluid, the light could travel exactly the same way back to the infinite in-line system. A CCD camera in the back captures the light and transfers it into electrical signals which could be analyzed by software. This technique although easily performed in a lab environment, requires the use of sophisticated optical systems and an optical table preventing the development of a portable device.

Figure 19: Transparent Indenter Measurement (TIM) System

The indentation fracture method provides a simple and fast measurement of the fracture toughness of brittle materials. In this method a sharp, Vickers indenter is pressed onto the sample surface with a weight of 200-3000 g. It results in an indentation with cracks emanating from the corners, as shown in the Figure 20. By measuring the size of the indentation, to determine the material's hardness, and by measuring the length of the cracks, the fracture toughness can be estimated.

Figure 20: (a) Vickers indenter used for indentation fracture toughness testing; (b) Indentation and cracks emanating from corners

A detailed description of the mechanics and experimental observations related to indentation fracture was done previously [33]. The cracks formed during indentation can be considered as a pair of orthogonal half-penny cracks,

diameter $2c$, wedged open in their center by a point force. The point force is due to the residual stress field left behind due to inelastic deformation at the tip of the indenter. From dimensional analysis, the stress intensity factor is:

$$K_I = \frac{\chi P}{c^{\frac{3}{2}}} \quad (21)$$

The constant χ is a function of the indenter geometry, and the material's hardness as shown in Equation (22) [33].

$$\chi = \xi_0 (\cot \psi)^{2/3} \left(\frac{E}{H} \right)^{1/2} \quad (22)$$

Where the constant $\xi_0 = 0.032 \pm 0.002$ is found by fitting experimental data, ψ is the half angle of the indenter, 68° , E is the Young's modulus, and H is the hardness. The Vickers hardness is found from

$$H_v = 1.854 \frac{W}{(2a)^2} \quad (23)$$

Where W is the applied load (kgf) and $2a$ is the indentation diagonal (mm). This is converted to true hardness in GPa by [34]

$$H = 1.057 \times 10^{-2} H_v \quad (24)$$

In equation (21), P is in N, not kgf. $P = Wg$, where g is the acceleration of gravity. [35]

4.3.1 Right Angle Mirror

With protected gold coating, the mirror (Figure 21) reflects the incident light with 90° angle and can be easily mounted in the optical system.

Figure 21: Right Angle Mirror [From Edmund Optics]

4.3.2 Infinite In-Line System

The infinite in-line unit is used as a tunnel for the incident light to go through. Besides, it connects to microscope to form a way for light transmitting to the CCD camera. This CCD camera is able to converse the light signal into electrical response. With programmed software, the image could be represented on screen.

4.3.3 Refractive Index Liquid

Any liquid can be used for its optical properties, but in practice the need for stability, low toxicity, system compatibility, transparency, and low cost in addition to specific refractive index and dispersion values would make finding a suitable liquid a complicated task. Since the microscope focus on the indenter tip, the refractive index liquid is used to define a straight path for light hitting the sample surface. Copper foil is first applied on the biomass surface to intense reflection, yet refractive index liquid has instantaneously chemical reaction with copper and shows dark image. Then gold leaf is employed to replace copper foil and prevent chemical reaction.

Chapter 5: Results and Discussion

5.1 Grindability of Torrefied Biomass Materials

The Hardgrove Grindability Index (HGI) was developed in the 1930s to empirically measure the relative difficulty of grinding coal to suitable small particle size (less than 300 micron) necessary for complete combustion in pulverized coal boilers. Therefore, the need to establish a true grindability index for torrefied biomass materials similar to that of HGI for coal exists [2]. Grindability is an important index of biomass materials which provides the information about energy consumption during size reduction of biomass materials. Through size reduction, torrefied biomass materials are able to be co-fired with coal particles for power generation. Riffle is applied to split whole biomass samples to check the density before the grinding test. Table 3 gives the density result of torrefied pine. Uniform size distribution of biomass sample is assumed to be achieved based on less than 2% standard deviation. The grinding curve represents the relation between energy consumption and particle size as shown in Figure 22 and Figure 23. It is a logarithm relation with 212 microns mesh applied as the final mesh of undersize material. From linear relationship of logarithm grinding curves between percentage of undersize material and grinding time, t_s are found as initial grinding time as shown in Table 6.

Table 3: Density Result of Torrefied Sample

Sample	Dark Pine Density (g/ml)	Light Pine Density(g/ml)
1	0.319	0.274
2	0.327	0.276
3	0.324	0.269
4	0.316	0.266
5	0.315	0.267
6	0.314	0.273
7	0.328	0.269
8	0.324	0.272
Average	0.321	0.271
Standard Deviation	1.74%	1.31%

In order to find equilibrium time which produces about 25% percent undersize materials, a rule needs to be followed to apply grinding time each time. And the formula is as below:

$$t_{i+1} = \frac{\ln 25}{\ln X_n}(t_i - t_n) + t_s, (i \geq 1), t_{i=0} = t_{i=1} = t_s \quad (25)$$

Table 4: 3.35mm Dark Pine Test Result

Test	Grinding time(min)	Mass of Undersize Mill 1(g)	Mass of Undersize Mill 2(g)	Mass of Undersize Mill 3(g)	Mass of Undersize Mill 4(g)	Average (g)	Deviation/g
0	1.77	14.711(25.53%)	15.133(26.27%)	13.800(23.95%)	15.529(26.48%)	14.726(25.56%)	0.660
1	1.77	7.708(13.38%)	8.024(13.93%)	8.264(14.43%)	8.456(14.68%)	8.113(14.08%)	0.323
2	3.09	8.475(14.71%)	8.535(14.81%)	8.366(14.52%)	8.943(15.52%)	8.580(14.89%)	0.252
3	5.27	10.108(17.54%)	10.345(17.96%)	9.833(17.15%)	10.935(18.98%)	10.318(17.91%)	0.453
4	7.25	11.569(20.08%)	12.164(21.11%)	11.311(19.63%)	12.638(21.93%)	11.921(20.69%)	0.597
5	8.64	11.573(20.09%)	12.556(21.79%)	12.618(21.90%)	12.816(22.24%)	12.391(21.51%)	0.556
6	9.92	12.705(22.05%)	13.015(22.59%)	12.305(21.36%)	12.723(22.08%)	12.687(22.02%)	0.292
7	11.08	12.914(22.41%)	12.632(21.92%)	13.300(23.08%)	12.705(22.05%)	12.888(22.38%)	0.300
8	12.16	13.598(23.60%)	13.609(23.62%)	13.933(24.18%)	13.469(23.38%)	13.652(23.70%)	0.198
9	12.74	13.318(23.12%)	13.074(22.69%)	13.913(24.15%)	13.240(22.98%)	13.386(23.23%)	0.366
10	13.52	14.016(24.33%)	14.469(25.16%)	15.027(26.08%)	14.489(25.15%)	14.507(25.18%)	0.413

Table 5: 3.35mm Light Pine Test Result

Test	Grinding Time/min	Mass of Undersize Mill 1(g)	Mass of Undersize Mill 2(g)	Mass of Undersize Mill 3(g)	Mass of Undersize Mill 4(g)	Average/g	Deviation/g
0	11.00	13.186(27.12%)	15.070(31.00%)	15.103(31.07%)	15.167(31.20%)	14.632(30.10%)	0.965
1	11.00	6.811(14.01%)	6.839(14.07%)	7.574(15.58%)	7.461(15.34%)	7.171(14.75%)	0.403
2	20.72	7.576(15.58%)	8.030(16.52%)	8.039(16.54%)	7.937(16.33%)	7.596(16.24%)	0.218
3	30.69	8.659(17.81%)	8.721(17.94%)	8.794(18.09%)	8.925(18.36%)	8.775(18.05%)	0.114
4	39.80	8.978(18.47%)	8.934(18.38%)	8.912(18.33%)	9.004(18.52%)	8.957(18.42%)	0.042
5	49.38	9.682(19.92%)	8.968(18.45%)	9.627(19.80%)	9.532(19.61%)	9.452(19.44%)	0.329
6	58.27	10.440(21.47%)	10.298(21.18%)	10.545(21.69%)	10.227(21.04%)	10.378(21.35%)	0.143
7	64.54	11.793(24.26%)	11.088(22.81%)	12.247(25.19%)	11.400(23.44%)	11.632(23.93%)	0.501
8	66.45	11.825(24.32%)	11.371(23.39%)	11.812(24.30%)	11.470(23.59%)	11.620(23.90%)	0.233
9	68.44	11.802(24.28%)	12.000(24.68%)	11.742(24.15%)	11.784(24.24%)	11.832(24.34%)	0.115

Hybrid Work Index (HWI) combines Bond's Work Index with Resistance to Impact Milling. W_i is the work index in Equation (26). For this research Equation (3) is modified for 25% undersize materials passing to derive Equation (26).

$$\frac{W}{W_i} = \frac{\frac{1}{\sqrt{P_{25}}} - \frac{1}{\sqrt{F_{25}}}}{\frac{1}{\sqrt{212}} - \frac{1}{\sqrt{\infty}}} \quad (26)$$

Grinding Curves of Torrefied Pine

Figure 22: m_i vs. $\sum_0^i t_i$ Grinding Curve of 3.35mm Torrefied Pine

Figure 23: m_i vs. $\sum_0^i t_i$ Logarithm Curve of 3.35mm Torrefied Pine

Here the product size is the cut size of the final mesh, i.e. 212 microns and feed size is the initial size of the biomass sample, i.e. 3.35 mm, HWI can be determined by plugging these sizes into Equation (26).

$$\frac{W}{W_i} = 1 - \frac{\sqrt{212}}{\sqrt{3350}} \quad (27)$$

Where W_i is the HWI and W is the grinding energy (power multiplies equilibrium time). In this research, power is 144 watts under defined working condition of ball-milling equipment. The equilibrium condition is assumed to be reached when the last three averaged percentages of undersize materials is within 90% of each other. According to Table 4 and Table 5, the equilibrium time is calculated via the iteration formula based on the last iteration of the whole test. Table 6 provides the result of torrefied pines. It is event that dark pine has undergone more torrefaction than light pine, and thus requires much less energy to grind to a defined size. Hybrid Work Index is calculated to effectively represent grindability of these two materials. This index could potentially develop into a standard for grinding of torrefied biomass materials.

Nevertheless, during the grinding process, untorrefied and partially torrefied biomass materials are discovered among the torrefied biomass materials as shown in Figure 24. Cross-section images shown in Figure 25 clearly demonstrate the existence of untorrefied materials and partially torrefied materials. Due to large-scale torrefaction of biomass, there are always some materials surrounded by other biomass which couldn't receive heat transfer from inert gas or other media. Size of untorrefied materials remains the same throughout the ball-milling process resulting in waste of grinding energy without size reduction. Thus, improving torrefaction condition is necessary. Rotating chamber or blades could utilize in the torrefaction process to dispense heat evenly to biomass materials. Another way is to pick out these untorrefied biomass materials before doing test and recycle them to torrefaction chamber in order to save energy.

Figure 24: Left: Untorrefied Pine; Middle: Partially Torrefied Pine; Right: Torrefied Pine

Figure 25: Cross Section of Torrefied Pine. Left: Untorrefied Pine; Middle: Partially Torrefied Pine; Right: Torrefied Pine

Table 6: Test Result of Torrefied Pine

Torrefied Pine	t_s/min	Equilibrium Time/min	Hybrid Work Index/KJ
Dark Pine	1.77	13.43	155
Light Pine	11.00	69.66	804

5.1.1 Energy Consumption

Figure 26: Power Consumption as A Function of Final Particle Size (Torrefaction Conditions in Brackets, Temperature in °C, Residence Time in Minutes) [3]

Figure 26 shows the power consumption required for size reduction of biomass. As shown, torrefied wood and coal requires the least and untreated biomass has much higher power consumption, with bone dry biomass situated in between [3]. According to other paper, 95% of coal particles can be combusted completely if the particle size is smaller than 300 microns [2]. In the early period of this research, torrefied biomass materials are received from NETL and run through the ball - mill instrument to reach less than 300 microns particle size. By recording the ball-milling time, energy consumption after size reduction can be calculated. Base on Table 7, a huge gap of torrefied biomass materials is discovered between 280°C and 200°C. And energy consumption varies with different kinds of samples. As torrefaction temperature reduces, energy consumption increases. Due to the power of the ball-milling machine is 144 watts, the energy consumption of torrefied biomass materials is able to be calculated as shown in Figure 27.

Table 7: Grinding Time of Torrefied Biomass Materials

Material	Ball-milling time required to grind the biomass materials to have all the particles with diameter less than 300 microns
Cherry Wood chips 280°C 1hr	6 minutes
Cherry Wood chips 200°C 1hr	3.5 hours
Bark 280°C 1hr	30 minutes
Bark 200°C 1hr	1.5 hours
Southern Pine	18 minutes
Switch Grass 280°C 1hr	18 minutes
Switch Grass 200°C 1hr	2 hours
Switch Grass 100°C 1.5hr	3 hours

Energy Consumption of Torrefied Biomass Materials

Figure 27: Energy Consumption of Torrefied Biomass Materials

5.1.2 Particle Size Distribution and Shape

Figure 28: (a) Cherry Wood Chips 280°C 1hr; (b) Cherry Wood Chips 280°C 1hr, 6min

Milling ; (c) SEM Picture of Particles after Milling

Figure 29: (a) Cherry Wood Chips 200°C 1hr; (b) Cherry Wood Chips 200°C 1hr, 3.5hr Milling; (c) SEM Picture of Particles after Milling

Figure 30: (a) Bark 280°C 1hr; (b) Bark 280°C 1hr, 30min Milling ; (c) SEM Picture of Particles after Milling

Figure 31: (a) Bark 200°C 1hr; (b) Bark 200°C 1hr, 1.5hr Milling; (c) SEM Picture of Particles after Milling

Figure 32: (a) Switch Grass 280°C 1hr; (b) Switch Grass 280°C 1hr, 18min Milling; (c) SEM Picture of Particles after Milling

Figure 33: (a) Switch Grass 200°C 1hr; (b) Switch Grass 200°C 1hr, 2hrs Milling; (c) SEM Picture of Particles after Milling

Figure 34: (a) Switch Grass 100°C 1.5hr; (b) Switch Grass 100°C 1.5hr, 3hr Milling; (c) SEM Picture of Particles after Milling

Figure 35: (a) Southern Pine; (b) Southern Pine, 18min Milling; (c) SEM Picture of Particles after Milling

5.2 Mechanical Property Evaluation of Torrefied Biomass Materials

Grindability test procedure is very complicated which is the reason of mechanical property evaluation. If a relation between these two properties can be established, the grindability measurement would become much simple.

5.2.1 Hardness

Figure 36: Typical Hardness Test on Torrefied Biomass Material

Figure 37: Hardness Value of Torrefied Biomass Materials

5.2.2 Elastic Modulus

(a)

(b)

Figure 38: Typical Experimental Result from A Micro-Indentation Test on Torrefied Biomass Materials. (a) Experimental Load-Displacement Curve Obtained with Multiple Partial Unloading; (b) Linear Relationship Observed between $dh(\text{total})/dp$ and $P^{(-1/3)}$

Figure 39: Elastic Modulus of Torrefied Biomass Materials

Table 8: Hardness Values of Torrefied Southern Pine Samples

Hardness (25gr)	Light Pine	Dark Pine
1	0.9	1.7
2	0.8	1.9
3	1.3	2.3
4	0.9	1.8
5	1.0	1.9
6	1.6	2.3
7	1.0	3.0
8	1.0	1.9
9	1.0	2.0
10	1.0	2.2
Average	1.1	2.1
Deviation	0.2	0.4

These two kinds of torrefied pine are provided by NETL and Manufactured by NCSU for grindability test. The Dark Pine is torrefied better than Light Pine. As a result, hardness value and Young's Modulus of Dark Pine is larger than Light Pine in Table 8 and Table 9.

Table 9: Young's Modulus Values of Torrefied Southern Pine Samples

Young's Modulus	Light Pine	Dark Pine
1	0.159	1.284
2	0.343	0.908
3	0.208	1.152
4	0.405	1.466
5	0.305	0.775
6	0.620	0.572
7	0.320	0.663
8	0.300	0.676
9	0.266	1.092
10	0.339	0.722
11	0.384	0.617
12	0.335	0.652
13	0.496	1.248
14	0.312	0.663
15	0.191	0.680
16	0.464	0.667
17	0.405	0.744
18	0.468	0.695
19	0.442	0.717
20	0.545	0.839
Average	0.365	0.842
Deviation	0.118	0.260

5.2.3 Fracture Toughness

One major problem to conduct fracture toughness tests on torrefied biomass materials is the difficulty to obtain clear images due to the non-reflective opaque surface of the biomass sample. To overcome this problem, thin brass strips (thickness: 2.5 microns and 5 microns) were applied to bond on the sample surface for enhanced reflectivity; the results were not satisfied due to chemical corrosion on the brass strip by the index matching fluid used in micro-indentation testing. The thin gold leaf is utilized to replace brass to prevent chemical corrosion (available at local art and craft shops). During this research period, a procedure to bond gold leaf ($\sim 0.125 \mu\text{m}$) on biomass samples has successfully developed without epoxy, as shown in Figure 40. Figure 41 shows a preliminary fracture toughness test plot using WVU load-based micro-indentation test method. As shown in Figure 42, crack occurred at the third stage of unloading. It shows the profile of Vickers indentation of the torrefied southern pine sample, the diagonal length is $\sim 1.33 \text{ mm}$ and the crack length is $\sim 0.392 \text{ mm}$. The fracture toughness value is estimated to be $0.11 \text{ MPa} \cdot \text{m}^{1/2}$. Unfortunately, there is only one test that crack happens with the apparent load drop during the indentation test.

Figure 40: Torrefied Southern Pine Specimen Bonded with Thin Gold Leaf ($\sim 0.125\ \mu\text{m}$)

Figure 41: Vickers Indentation Load-Depth Plot of Torrefied Southern Pine (Crack Happens around 28 N due to Load Drop)

Figure 42: Vickers Indentation for Fracture Toughness Measurement of Torrefied Southern Pine (Indented Diagonal Length: $\sim 1.33\ \text{mm}$, Crack Length: $\sim 0.392\ \text{mm}$)

5.3 Torrefaction of Raw Biomass Material

Before any torrefaction test is carried out, the WVU torrefaction unit had been under diagnostic testing for over a month. Several shakedown tests had been done and accurate temperature control is the major issue. First, several closed-loop control temperature tests were attempted; however, the variation of the temperature is over 30°F which would not be appropriate for torrefaction test. Then, proportional voltage output control is another choice to keep the temperature increments in a certain range. And two torrefaction tests on cherry wood chips had been done with this method to demonstrate the feasibility of this torrefaction system. Regarding the first test, the pre-heater was heated and maintained at 280°C and due to the heat loss between the pre-heater and the torrefaction tube chamber, gas temperature drops to 235°C at the torrefaction chamber. About the second test, the pre-heater was heated and maintained at 340°C such that the tube chamber was stable at 290°C. The temperature variation is less than 5°C for both tests which is tolerable in torrefaction.

Figure 43: Pictures of Cherry Wood Chips. (a) Before Torrefaction; (b) Torrefaction Condition: 235°C, 1hr; (c) Torrefaction Condition: 290°C, 0.5hr

Table 10: Weight Loss of Torrefied Cherry Wood Chips under Different Torrefied Condition

Torrefaction Condition of Cherry Wood Chips	Mass(before torrefaction)/g	Mass(after torrefaction)/g	Weight Loss/%
235°C, 1hr	2.486	1.834	26.2
290°C, 0.5hr	2.139	0.776	63.7

As torrefaction temperature increases, cherry wood chips become darker and have more weight loss. Weight loss of torrefied biomass is generally between 20% and 40%. So 290°C is too high for torrefaction of cherry wood chips. Too high temperature would result in gasification which reduces the energy density.

Table 11: Hardness of Torrefied Cherry Wood Chips

Hardness of Cherry Wood Chips (25gr, Vickers)	235°C, 1hr	290°C, 0.5hr
1	4.2	3.4
2	4.6	7.1
3	5.4	5.8
4	8.3	7.7
5	6.0	3.2
6	6.7	4.0
7	5.8	3.3
8	7.3	5.2
9	6.9	4.7
10	8.2	4.2
Average	6.3	4.9
Deviation	1.	1.6

Table 12: Young's Modulus of Torrefied Cherry Wood Chips

Young's Modulus of Cherry Wood Chips (GPa)	235°C, 1hr	290°C, 0.5hr
1	1.193	0.416
2	0.902	0.381
3	0.714	0.423
4	0.904	0.269
5	0.541	0.360
6	0.655	0.200
7	1.714	0.251
8	1.180	0.083
9	0.870	0.340
10	0.972	0.239
11	1.089	0.330
12	0.941	0.292
13	0.907	0.391
14	1.027	0.142
15	1.024	0.305
16	0.755	0.110
17	1.915	0.049
18	1.060	0.208
19	1.210	0.232
20	1.834	0.160
Average	1.070	0.259
Deviation	0.369	0.112

Biomass material with a high torrefaction temperature has low hardness and Young's Modulus value compared to biomass under low torrefaction temperature condition because hemicellulose which connects the fibers breaking down during torrefaction. The higher the temperature reaches, the more hemicellulose decompose. Without these connecting parts, the biomass turns into loose.

Figure 44: (a) Raw Cherry Wood Chips; (b) N₂ Flow Rate: 18000sccm; (c) N₂ Flow Rate: 100sccm; (d) N₂ Flow Rate: 0sccm

Table 13: Physical Property of Torrefied Cherry Wood Chips

Torrefaction Condition	Mass(before torrefaction)	Mass(after torrefaction)	Mass loss	Density(before torrefaction)	Density(after torrefaction)	Density Increase
0sccm N ₂	38.550g	11.574g	69.98%	0.145g/ml	0.218g/ml	50.34%
100sccm N ₂	33.127g	10.022g	69.75%	0.145g/ml	0.245g/ml	68.97%
18000sccm N ₂	36.303g	11.316g	68.83%	0.145g/ml	0.221g/ml	52.41%

Table 14: Grinding Test Result of Torrefied Cherry Wood Chips

6min Grinding	>850μm/g	425-850μm/g	212-425μm/g	<212μm/g
0sccm N ₂	8.018(74.10%)	1.514(13.99%)	0.577(5.33%)	0.711(6.57%)
100sccm N ₂	7.321(73.82%)	1.557(15.70%)	0.512(5.16%)	0.527(5.32%)
18000sccm N ₂	0.402(4.40%)	0.200(2.19%)	1.187(13.00%)	7.345(80.41%)

Torrefaction, as a heat treatment process depends on temperature and time. Previous research shows that the yield of solid product decreases while the yield of gas, tar and water increases with the temperature and the residence time and it is not found a strong influence of the inert gas flow on the product distribution at the selected conditions. The content of carbon in the solid product increases at higher temperature of the torrefaction and longer residence time while the content of hydrogen and oxygen decrease, increasing the calorific value of the torrefied biomass [12]. Furthermore, due to the huge flow rate of nitrogen (N₂), large amount of N₂ waste during torrefaction test. For this reason,

three tests were carried out to study the influence of flow rate of N_2 . Table 13 proves that flow rate of N_2 doesn't affect the physical property of torrefied cherry wood chips, such as mass loss and density. And all these biomass materials are completely torrefied shown in Figure 44. Nevertheless, from Table 14, after 6min of ball-milling, size distribution of these biomass materials is dissimilar to each other. 80 percent of torrefied cherry wood chips under 18000sccm N_2 are less than 212 microns while under 100sccm N_2 or without N_2 , only 5 or 6 percent materials are less than 212 microns. Part of the reason is that the heat transfer coefficient of forced convection is much larger than free convection. Nitrogen could easily transfer heat into the inner part of biomass and more hemicellulose is broken down. Since the flow rate of previous tests done by other researchers is less than 2000sccm. According to the result of flow rate of 18000sccm, grindability of torrefied biomass materials improves greatly. Therefore, inert gas flow does increase the grindability of torrefied biomass materials, but not the physical property of torrefied biomass materials.

5.4 Solar Torrefaction System

Convection heat transfer via inert gas flow is the most common technique used for the torrefaction of biomass materials. However, using any type of inert gas or steam involves large containment system with large amounts of surface area, high equipment costs, high energy costs, slow treatment rates, and low overall operating efficiencies with resultant high production costs. Maintaining an oxygen free inert gas environment to these systems adds to the complexity and costs [36]. The development of a solar torrefaction system would alleviate much of this cost and is a novel approach for breaking down hemicellulose in biomass materials via a renewable energy source. Efficiently converting radiant energy generated by the sun, solar evacuated tubes have been shown to be an effective and low cost hot water heater used worldwide. In this research, an evacuated tube's ability to proficiently perform torrefaction of biomass materials has been investigated, where tar and excess gas emitted by these materials at elevated temperatures was periodically removed via a timed mechanical pump.

Figure 45: Flow Chart of Solar Torrefaction System

As Figure 45 shows, biomass materials are inside the solar evacuated tube. Rotating joint is designed for solar evacuated tube rotating during the torrefaction process in order to evenly distribute radiant heat. Rotation can be done by adding an electric motor on the other side of the solar evacuated tube. A thermocouple is inside the solar evacuated tube and temperature data could be collected by a temperature data logger. The vacuum pump is for driving air and torrefied gas out of the solar evacuated tube. This pump is controlled by a timer which can program to be turned on for a certain time in a defined period. Considering the safety issue, a check valve added at the end in case pressure builds up inside and break the tube.

Several tests have been carried out after the solar torrefaction system was constructed. Depending on the weather condition, sometimes highest temperature can shoot up to 300°C and stay above 250°C for four hours in one day. Figure 46 is one test that has been done for three days. Temperature lasts for three hours in both two different days which higher than 250°C. Cherry wood chips are totally torrefied both on the surface and the inner part. Due to the structure reason, cherry wood chips in the bottom part of solar evacuated tube don't receive much heat during the solar torrefaction process; thus, it is only

partially torrefied. Table 15 gives an estimate of grindability of torrefied cherry wood chips via solar system compared to Dark Pine and Light Pine. However, large amounts of tar are produced during the torrefaction process. There is tar inside the 1/4inch pipe between solar evacuated tube and the vacuum pump. Since 1/4inch tube from the exit of the vacuum pump is clean, most of tar must accumulate in the pump. System cleaning would become an issue. Most of the system parts are difficult to clean, such as solar evacuated tube, 1/4inch pipe and vacuum pump. The whole system requires maintenance after certain period of work.

Table 15: Grinding Test Result of Torrefied Cherry Wood Chips via Solar System

6min Grinding	>850 μ m/g	425-850 μ m/g	212-425 μ m/g	<212 μ m/g
Torrefied cherry wood chips	1.790(11.35%)	1.171(7.43%)	3.929(24.92%)	8.879(56.31%)
Partially torrefied cherry wood chips	5.561(29.54%)	2.715(14.42%)	4.277(22.72%)	6.236(33.13%)
Dark Pine	0.587(5.43%)	0.317(2.93%)	1.138(10.53%)	8.767(81.11%)
Light Pine	3.545(47.26%)	0.992(13.22%)	0.681(9.08%)	2.283(30.44%)

**Figure 46: Temperature of Solar Torrefaction System. Left: Raw Cherry Wood Chips;
Middle: Torrefied Cherry Wood Chips; Right: Partially Torrefied Wood Chips**

Chapter 6: Conclusion and Recommendation

6.1 Influence of Torrefaction Condition

Several torrefaction tests have been carried out to study the influence of torrefaction condition on grindability of biomass. Between 200 and 300°C, the higher the temperature and longer the time are, more hemicellulose breaks down which improves grindability of biomass. However, high temperature and long time mean large energy consumption which creates high manufacturing cost. Moreover, previous research shows no influence of flow rate of inert gas, however, the flow rate in these researches doesn't exceed 2000sccm. When the flow rate reaches 18000sccm, grindability of the torrefied biomass materials significantly improves. Therefore, the requirement of a proper torrefaction condition for each biomass does exist. It would be beneficial for industrial manufacture.

6.2 Hybrid Work Index

A modified BWI procedure was utilized with Resistance to Impact Milling (RIM) to evaluate torrefied biomass materials and establish a Hybrid Work Index (HWI) for assessing the grindability of biomass materials. The hybridized procedure has been shown to be both highly correlated to energy consumption and sensitive to degree of torrefaction. The proposed HWI is certainly useful for assessing torrefaction in a laboratory environment, but it may also correlate to grinding energy at industrial scales.

6.3 Particle Shape of Torrefied Biomass Materials

SEM pictures indicate most of particle shape produced by ball-milling instrument is free geometry. Spherical particles would be ideal for combustion, yet most of the particles are not close to sphere. More spherical particles should be produced if more hemicellulose breaks down.

6.4 Mechanical Property Measurement

A relation between mechanical property and grinding efficiency is established for the same biomass material. From Young's modulus and hardness test results, biomass material with high torrefaction temperature has lower Young's Modulus and hardness value. Once more, torrefaction breaks down hemicellulose and looses material in result of low hardness and Young's modulus value. This mechanical property evaluation method could possibly be utilized by industry for biomass grindability measurement which is simple and cheap.

6.5 Recommendation for Future Work

After the Entrained Gas-Flow Torrefaction System was built up in the high bay area of NRCCE, there is not enough time to perform plenty of torrefaction tests. Information about proper temperature and time of each biomass material hasn't been found, yet it is valuable for industrial manufacture. More tests need to be carried out with different temperature and time. Moreover, grinding efficiency of biomass materials with different torrefaction condition requires to be compared to each other.

Solar Torrefaction System is another direction of future research. Since solar energy is free, the cost of manufacturing torrefied biomass materials would highly decrease. The current solar torrefaction system in our lab is simple and immature; many problems arise during the test. However, with proper design, these problems may be solved. Therefore, it is worth spending time on this research in the future.

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