Biomass Properties and Handling

Learning Objectives:

- Enhance participant understanding of the opportunities and challenges of using biomass as a feedstock for energy, food and materials.
- Enhance participant familiarity with biomass property terminology.
- Provide participants with opportunity to gain hands-on experience in measuring biomass properties.
- Provide participants with opportunity to gain hands-on experience in biomass handling.

Learning Outcomes:
Upon completion of this lab, participants will be able to:

- List and describe current and potential future uses for biomass.
- Describe the opportunities and challenges associated with using biomass as a feedstock.
- Describe the various components of biomass.
- Measure biomass physical and chemical properties.
- Explain the significance of the biomass property measurements used.
- Calculate the volumetric energy density of various fuels from measurement data.
- Determine the identity of a biomass sample based on its properties.

Pre-Lab

Background

What is biomass?

Biomass is material that is derived from living or recently living biological organisms. In the energy context it is often used to refer to plant material, however by-products and waste from livestock farming, food processing and preparation and domestic organic waste, can all form sources of biomass. Biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including atoms of oxygen, often nitrogen and also small quantities of other atoms, including alkali, alkaline earth and heavy metals.

Plants use the light energy from the sun to convert water and carbon dioxide to sugars that can be stored, through a process called photosynthesis. Researchers study how the sugars in the biomass can be converted to more usable forms of energy like electricity and fuels. Some plants, like sugar cane and sugar beets, store energy as simple sugars. Other plants store the energy as more complex sugars called starches. These plants include grains like corn. All of these are also used for food.

Another type of plant matter, called cellulosic biomass, is made up of very complex sugar polymers, and is not generally used as a food source. Cellulosic feedstocks under consideration for biofuels include:

- Agricultural residues (leftover material from crops, such as the stalks, leaves, and husks of corn plants)
- Forestry wastes (chips and sawdust from lumber mills, dead trees, and tree branches)
- Municipal solid waste (household garbage and paper products)
- Food processing and other industrial wastes (black liquor, a paper manufacturing by-product)
- Energy crops (fast-growing trees and grasses) developed just for this purpose

The main components of these types of biomass are:

- Cellulose is the most common form of carbon in biomass, accounting for 40%-60% by weight of the biomass, depending on the biomass source. It is a complex sugar polymer, or polysaccharide, made from the six-carbon sugar, glucose. Its crystalline structure makes it resistant to hydrolysis, the chemical reaction that releases simple, fermentable sugars from a polysaccharide.

- Hemicellulose is also a major source of carbon in biomass, at levels of between 20% and 40% by weight. It is a complex polysaccharide made from a variety of five- and six-carbon sugars. It is relatively easy to hydrolyze into simple sugars but the sugars can be difficult to ferment.

- Lignin is a complex polymer, which provides structural integrity in plants. It makes up 10% to 24% by weight of biomass. It remains as residual material after the sugars in the biomass have been converted. It contains a lot of energy and can be burned to produce steam and electricity for biochemical biomass processing.

Why use biomass?

Biomass is an attractive energy source for a number of reasons.

- The use of biomass energy has the potential to greatly reduce greenhouse gas emissions. Burning biomass releases about the same amount of carbon dioxide as burning fossil fuels. However, fossil fuels release carbon dioxide captured by photosynthesis millions of years ago. Biomass, on the other hand, releases carbon dioxide that is largely balanced by the carbon dioxide captured in its own growth (depending how much energy was used to grow, harvest, and process the fuel).

- The use of biomass can reduce dependence on foreign oil because biofuels are the only renewable liquid transportation fuels available.

- Biomass energy supports U.S. agricultural and forest-product industries. The main biomass feedstocks for power are paper mill residue, lumber mill scrap, and municipal waste. For biomass fuels, the most common feedstocks used today are corn grain (for ethanol) and soybeans (for biodiesel). In the near future, agricultural residues such as corn stover (the stalks, leaves, and husks of the plant) and wheat straw will also be used. Long-term plans include growing and using dedicated energy crops, such as fast-growing trees and grasses, and algae. These feedstocks can grow sustainably on land that will not support intensive food crops.

Biomass has successfully been used before to supply energy and has the potential to do so again.

- Up until the 1860s, the U.S. used biomass (wood) for nearly 91% of all energy consumption.

- 14% of the world still utilizes biomass for energy.

- In a recent DOE study, a full 73% of all energy consumed by US manufacturing was through boilers and burners, principally powered by natural gas or fuel oil, but highly adaptable to solid fuel usage.

Biomass Challenges

There are several challenges associated with using biomass for energy, especially liquid transportation fuels.

- Biomass is seasonal; most energy and feedstock demands are continuous.
- Biomass is very heterogeneous and complex; properties of biomass can vary with the species of plant, the location in which it was grown, the growing conditions, the harvest and storage conditions, etc. The ability to consistently and accurately measure biomass properties is therefore critical to designing bioprocessing operations.
- Biomass has a relatively low energy density, meaning that it takes a lot more biomass to supply the same amount of energy as a traditional hydrocarbon fuel.
- The market for bio-based energy and other bio-based products (i.e. suppliers, buyers, distributors, prices, demand) is relatively undeveloped.

Heating Value

The heating value, in units of MJ/kg or BTU/lb or cal/g, is one of the most important characteristics of a fuel because it indicates the total amount of energy that is available in the fuel. Heating value is mostly a function of a fuel's chemical composition and can be expressed in two ways: the higher heating value (HHV) or the lower heating value (LHV). HHV is the total amount of heat energy that is available in the fuel, including the energy contained in the water vapor in the exhaust gases. LHV is the same as HHV except that it does not include the energy embodied in the water vapor. Generally, the HHV is the appropriate value to use for biomass combustion, although some manufacturers may utilize the LHV instead, which can lead to confusion.

The HHV for coal ranges from 20 to 30 MJ/kg (8600-12900 Btu/lb). Nearly all kinds of biomass feedstocks destined for combustion fall in the "as-received" (not oven dry) HHV range of 15-19 MJ/kg (6450-8200 Btu/lb) with 15-17 MJ/kg (6450-7300 Btu/lb) for most agricultural residues and 18-19 MJ/kg (7750-8200 Btu/lb) for most woody materials.

Moisture Content

Moisture content is one of the easier biomass properties to measure and can make the difference between a good and a bad fuel. High moisture fuels burn less readily and provide less useful heat per unit mass; this is because water itself provides no energy value and much of the energy in the fuel is used up to heat and vaporize water. Fresh, "green" wood is often about half water; many leafy crops are primarily water. On the other hand, extremely dry fuel can cause dust problems, leading to equipment fouling and potential explosion hazards. Moisture content can be calculated on two bases: wet or dry. In wet basis calculations, the moisture content is equal to the mass of water in the fuel divided by the total mass of the fuel. In dry basis calculations, the moisture content is equal to the mass of water in the fuel divided by the mass of the dry portion of the fuel. It is important to know which type of calculation is being used, as the two values can be quite different. For example, a 50% wet basis moisture level is the same as a 100% dry basis moisture level. Air-dried biomass typically has about 15-20% moisture, whereas the moisture content for oven-dried biomass is around 0%. Moisture content is also an important characteristic of coals, varying in the range 2-30%. The practical maximum moisture level for combusting fuel is about 60% (wet basis), although most commercial equipment operates with fuels that only have up to about 40 % moisture.

Figure 1 shows the typical range of HHV for some common biomass fuels. Note that wood (which has lower ash content) tends to have a slightly higher heating value than field crops. The HHV and LHV of wood fuel are shown in Figure 2 as a function of fuel moisture content.

Figure 1. Heat content of various fuels (oven dry). One MJ (megajoule) is enough energy to brew about 10 cups of coffee if your pot is 100 percent efficient. It is also equal to about 1,000 BTUs.

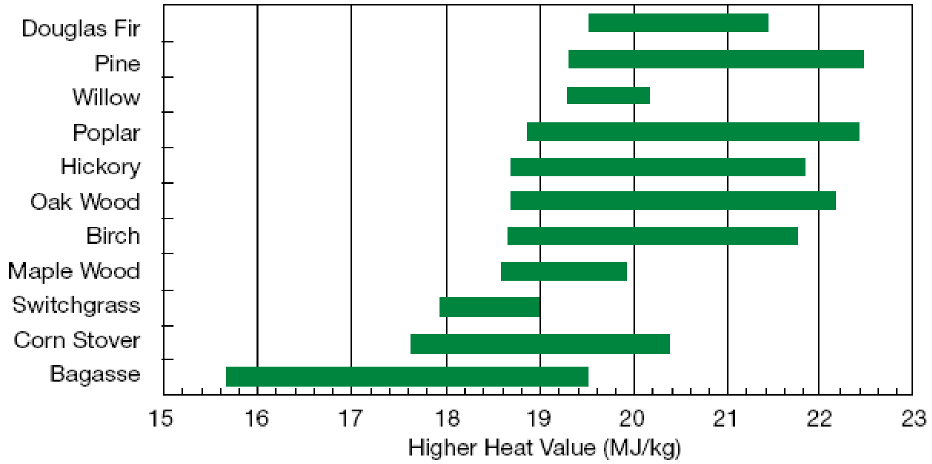
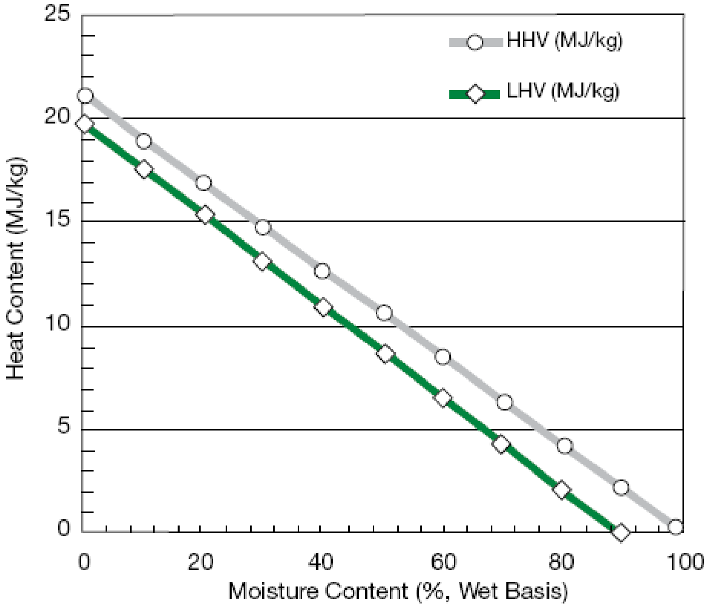


Figure 2. Typical biomass higher heating value and lower heating value versus moisture content.



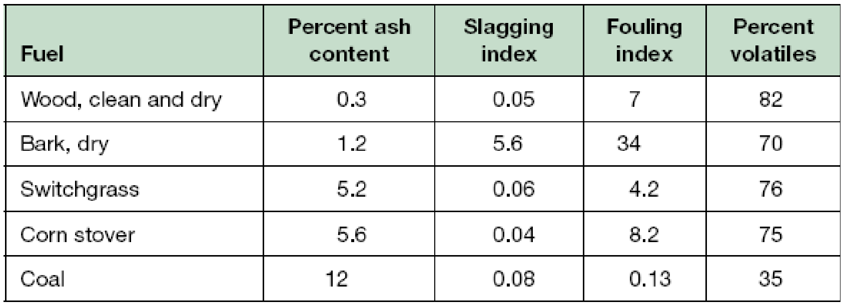
Composition

In addition to heating value and moisture content, three other biomass properties are significant to biomass' performance as a fuel: (1) ash content, (2) susceptibility to slagging and fouling, and (3) volatiles content. Ash content is the mass fraction of biomass composed of uncombustible mineral material. Grasses, bark, and field crop residues typically have much higher ash contents than wood. Systems that are designed to combust wood can be overwhelmed by the volume of ash if other biofuels are used.

Slagging and fouling are problems that occur if ash begins to melt during combustion, forming deposits on combustor surfaces (fouling) or leaving hard chunks of glassy material in the bottom of the combustion chamber (slag, aka "clinkers"). Certain mineral components in biomass fuels, primarily silica, potassium, and chlorine, can cause these problems to occur at lower temperatures than normal. Many studies have observed that the high mineral content in grasses and field crops can contribute to fouling and clinkering—a potentially expensive problem for a combustion system. The timing of harvest can affect this property, with late harvested crops having noticeably lower ash content (Adler et al., 2006). Dirt contamination also adds to the mineral content and associated slagging and fouling problems, so it is important that biomass feedstock be as "clean" as possible. Slagging and fouling is minimized by keeping combustion temperatures low. Alternately, some biomass combustion equipment is designed to encourage the formation of clinkers but is able to dispose of the hardened ash in an effective manner. Table 1shows a "slagging index" and a "fouling index" for several fuels, two measures that give some indication of the tendency of a fuel to form slag or foul a boiler. Values lower than 0.6 are preferable. These indices, however, were developed for coal combustion and their significance for biomass fuels is questionable. Treat these values with caution.

The volatiles content in a fuel is a lesser-known property that refers to the fraction of the fuel that will readily volatilize (turn to gas) when heated to a high temperature. Fuels with "high volatiles" will tend to vaporize before combusting ("flaming combustion"), whereas fuels with low volatiles will burn primarily as glowing "char." This affects the performance of the combustion chamber and should be taken into account when designing a combustor.

Table 1. Examples of ash, slagging, fouling, and volatiles.



Fuel	Percent ash content	Slagging index	Fouling index	Percent volatiles
Wood, clean and dry	0.3	0.05	7	82
Bark, dry	1.2	5.6	34	70
Switchgrass	5.2	0.06	4.2	76
Corn stover	5.6	0.04	8.2	75
Coal	12	0.08	0.13	35

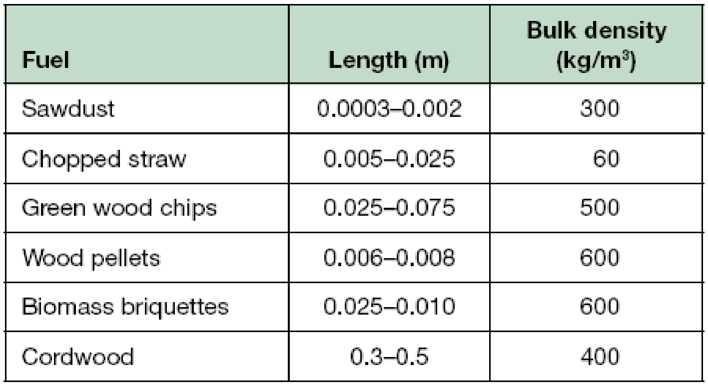
Fuel Size and Density

The particle size and density of biomass fuels are also important as they affect the burning characteristics, namely the rate of heating and drying during the combustion process. Fuel particle size also dictates the type of handling equipment required. The wrong size fuel will negatively impact combustion process efficiency and may cause jamming or damage to the handling equipment. Smaller-sized fuel is more common for commercial-scale systems because smaller fuel is easier to use in automatic feed systems and allows for finer control of the burn rate by controlling the rate at which fuel is added to the combustion chamber. Fuel particle size and density are probably the most overlooked factors affecting fuel performance and should be given careful consideration when selecting a fuel type. Bulk density is the mass of a material divided by the volume it occupies. Bulk density of granular materials is dependent on the manner in which it is handled. For example, freely settled material has a lower bulk density than tapped or compacted materials. Table 2 lists the size and bulk density of some common biomass fuels.

Angle of Repose

Angle of repose is the maximum angle that bulk granular materials will form when poured onto a horizontal surface due to particle size and frictional and cohesive forces between individual particles. The angle of repose of materials is important to the design of storage structures and material handling equipment.

Table 2. Typical size and density of biomass fuels.



Fuel	Length (m)	Bulk density (kg/m^3)
Sawdust	0.0003–0.002	300
Chopped straw	0.005–0.025	60
Green wood chips	0.025–0.075	500
Wood pellets	0.006–0.008	600
Biomass briquettes	0.025–0.010	600
Cordwood	0.3–0.5	400

Biomass vs. Fossil Fuels

The bulk density (and resulting energy density) of most biomass feedstocks is generally low, even after biomass densification: about 10- 40% of the bulk density of most fossil fuels, although liquid biofuels have comparable bulk densities.

Most biomass materials are easier to gasify than coal, because biomass is more reactive and has higher ignition stability. This characteristic also makes biomass easier to process thermochemically into higher-value fuels such as methanol or hydrogen. Biomass ash content is typically lower than for most coals, and sulphur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrients removed by harvest.

Among the liquid biomass fuels, biodiesel (vegetable oil ester) is similarity to petroleum-derived diesel fuel, apart from its negligible sulfur and ash content. Bioethanol has only about 70% the heating value of petroleum, but its sulfur and ash contents are also very low. Both of these liquid fuels have lower vapor pressure and flammability than their petroleum counterparts, an advantage in some cases (e.g. use in confined spaces such as mines) but a disadvantage in others (e.g. engine starting at cold temperatures).

Conclusion

Several characteristics affect the performance of biomass fuels, including the heating value, moisture content, ash content and chemical composition, particle size, and density of the fuel. These characteristics can vary noticeably from fuel to fuel and natural variations of a given fuel type can be significant. Combustion equipment can and should be designed to handle this range of properties.

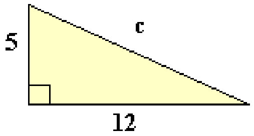
Pre-Lab Tasks

1. List two examples of agricultural biomass energy sources other than corn and soybeans?

2. Why are moisture, ash and volatiles contents important in combustion?

3. Describe the relationship between moisture content and heating value (LVH, HHV).

4. Why is fuel size important in combustion?
5. Determine value for c:



6. Convert units of energy 7841 cal/g to BTU/lb and to MJ/kg.
   Known relationships: 1BTU = 1055 J = 252 cal
   2.2 lbs = 1 kg

7. In making compost, the moisture of the resultant biomass mixture is a key critical factor to consider. 10g of grass clippings (W_w) are placed into a 4g container. After drying, the container plus clippings weighs 6.3g. Taking into account the 4g container, calculate the % moisture of the grass clippings using the following equation:

   $M_n = ((W_w - W_d)/W_w)) \times 100$

   M_n = moisture content (%) of material n
   W_w = wet weight of the sample
   W_d = weight of the sample after drying

   Instructor ((10-2.3)/10) x 100=77% for the grass clippings.

8. Calculate the annual cost for John to use a window fan. The local utility rate is 8.9 cents per kilowatt-hour (kWh), the window fan requires 200W and John runs the fan 4 hours per day.

   Note: power consumption (kWh) = power * hours used per day * days used per year

Annual Appliance Operating Cost

$$\frac{\text{Watts X Hours used per day X Days used per year}}{1000} = \text{Kilowatt-hour (kWh) Consumption}$$

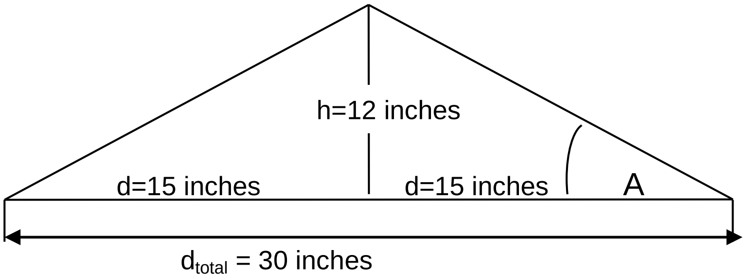
Multiply this number by your local utility's rate per kWh consumed (Assume the cost is 8.9 cents/kWh) to calculate annual cost.

Calculate the annual cost for John:
If John uses a window fan (200 watts) 4 hours a day for 120 days per year, how much does it cost him to run his fan per year?

$\frac{200 \text{ X } 4 \text{ X } 120}{1000}$ = 96 kWh (**Instructor)**

96 kWh X 8.9 Cents/kWh = $8.16 per year **(Instructor)**

9. Pencil sharpener shavings have spilled onto the desk top and you are curious about the shape (angle of repose) of the pile. Determine the internal angle, A, between the surface of the pile and the desk surface using the diagram below (imagine pile as two right triangles put together):



Instructor: Angle A: tan = 12/15 Angle A =39

10. In contracting a truck hauler for biomass, a company has hired a dump truck driver with a good sized bed: l=17', w=8'6", h=5'. What is the volume capacity of the dump truck bed in Liters?

Instructor: 17'x 8'6" x 5' = 722 cubic feet= 20, 444.2L

1

Lab Procedure Part 1: Biomass Characterization

Safety Checklist

- Proper attire is worn (long pants and closed-toe shoes).
- Food and drinks are stored and consumed outside the laboratory.
- Lab coat and safety glass are worn.
- Latex or nitrile gloves are used when handling samples and chemicals.

Problem Statement

Your team has been provided 2-3 bags of mysterious biomass, labeled accordingly. One bag contains biomass pellets. Your assignment is to characterize each biomass and construct a table of the biomass properties. Your characterization of the biomass will include: proximate analysis (moisture, volatiles, fixed carbon and ash content), bulk density, angle of repose, higher heating value, and volumetric energy density.

Proximate Analysis

Background

The Navas TGA-1000 (thermogravimetric analyzer) is basically a furnace and a scale; it is used to measure changes in weight associated with changes in temperature. The most common measurement performed on the TGA is proximate analysis: determining the moisture, volatile matter, fixed carbon, and ash content of a substance. Moisture content is the mass lost above 100°C. Volatile matter is the mass lost upon heating to high temperatures in an inert environment (here nitrogen). Ash content is the mass that remains after heating the sample to high temperatures in the presence of air. Fixed carbon content is determined by difference.

The TGA set-up consists of three parts: the compressed gas cylinders, the instrument with blower, and the computer with software to operate the instrument. The compressed gas cylinders include a compressed air tank used for the oxygen source, a nitrogen tank, and a compressed air tank shared with the bomb calorimeter and used to power the TGA pneumatics.

The relevant parts of the main instrument (Figure 1) include: lid, sample crucibles, carousel, test weight button, blower, and vent tubing. Lid height is controlled through pneumatics and has several levels including fully open, closed and partially open (for cooling). Reusable ceramic crucibles are used to hold the samples. The ceramic carousel consists of 20 slots that hold the reference and sample crucibles, and can be raised to rotate or lowered to place a sample on the weighing pedestal. "Home position" for the carousel is at the front of the instrument and is where the scale pedestal is located; it is labeled with an arrow on the white insulating material. The "test weight button" is the red button seen in Figure 2. It is used during sample loading and unloading

to lower and/or rotate the carousel. The blower and vent tubing is need to vent gases generated during the analysis into the fume hood.
The software is located on the desktop and under "Navas Instruments TGA." Instructions for using the software are located in the "Instrument Operation" section of this manual.

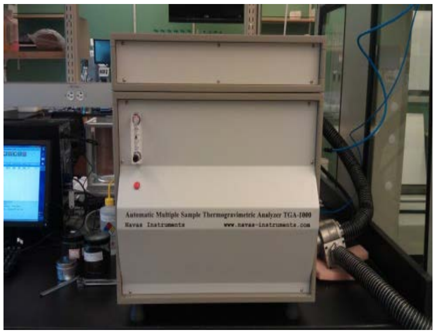


Figure 1

Figure 2

Figure 3

Pre-experiment Checklist

The following checklist is to be performed before using the TGA:

- **Samples to be tested are solids, not liquids.**
- Computer is on and the instrument software is open.
- Printer is on and has sufficient paper.
- Compressed air cylinder for pneumatics is open and set to 80 psi.
- Compressed air and nitrogen cylinders are open and set to approximately 60 psi and 50 psi, respectively.
- Fume hood is functioning as indicated by a green light on the upper right of the hood (green arrow in Figure 3).
- The vent tubing outlet is venting into the fume hood and is held in place by the fume hood sash (red arrow in Figure 3).
- Instrument lid is open.
- All crucibles have been removed from the carousel and cleaned.

Procedure

1. Click Options<Programs located on the toolbar at top. Choose Biomass ATSM program.
2. Once program is chosen, click Calibration<Diagnostics on the toolbar. The diagnostics window will pop up.
3. Without any crucibles in the carousel, click Close under Lid menu; once the lid is closed, click Tare button to zero out the scale.
4. Click on Weight icon. When prompted, enter the number of samples to be tested (not including the empty reference crucible). Carousel positions will appear to fill in carousel diagram indicating which slots are to be used in this analysis.
5. If the carousel is not already in home position, it will rotate there. Place the empty reference crucible in home position.

6. Press the red test weight button to rotate the carousel to the next position to be filled. Place an empty sample crucible in that position.
7. Repeat until all needed carousel positions are filled with empty crucibles. The lid should close automatically to measure and record the empty crucible weights, and then reopen so that the samples can be loaded.
8. During the loading process, each sample will need to be given an identifier and the crucible filled using the test weight feature as follows:
    a. For the first sample, first replicate, create a sample identifier by entering a group member's last name followed by 1 space 1 in the prompt box. The next replicate will be the name followed by 1 space 2.For example:
        Ramirez 1 1 (Ramirez' first sample, second replicate)
        Ramirez 1 2 (Ramirez' first sample, second replicate)
    b. Remove sample crucible from carousel and fill it with the desired amount of sample (this can be approximate for now).
    c. Return sample crucible to its place on the carousel and press the red test weight button; this will lower the carousel, setting the crucible on the balance pedestal. The current weight of sample will be displayed.
    d. To change the mass of sample, remove crucible from carousel and add/remove appropriate amount; return sample to carousel to reweigh (do not press red button again as this will move on to the next sample).
    e. Once the amount of sample is correct, press ENTER key to move on to the next sample.
    f. Repeat until three replicates for each sample are identified and loaded.
    g. Press ENTER key to continue.
9. The instrument will automatically close the lid and reweigh the samples.
10. Once the samples have been reweighed with the lid closed and the analysis is ready to run, click the Execute (traffic light) icon.
11. A message will be displayed asking to regulate air flow. Adjust the flow meter on the front of the instrument to be between 4 and 6 L/min, and click okay.
12. The instrument will now run through the selected analysis program (may take several hours).
13. If the analysis cycle was completed successfully, the computer will automatically print the data in the preset format selected when creating the program, as well as any requested graphs. The lid will gradually raise and the blower/internal fans turn on and off to complete an automated cooling cycle.
14. Only when the lid is completely open and the furnace has cooled to 40°C should crucibles be removed for cleaning.

Data Analysis

1. Calculate the fixed carbon content for each replicate.
2. Calculate the average moisture content, volatiles content and ash content. Make note of any replicates that had significantly different data.
3. Calculate the average volatiles, fixed carbon and ash content of the sample on a dry basis using the following formula:
    % dry basis = % wet basis * (100/(100 – moisture content %))

Bulk Density and Angle of Repose

Background

Bulk density is defined as the weight per unit volume of material. It provides a gross measure of particle size and dispersion which can affect material flow consistency and reflect packaging quantity. The angle of repose or, more precisely, the critical angle of repose, is the steepest angle of descent or dip of the slope relative to the horizontal plane when material on the slope face is on the verge of sliding. This angle is given by the number (0°–90°).

When bulk granular materials are poured onto a horizontal surface, a conical pile will form. The angle of repose, or angle with a horizontal surface formed when free-flowing grain comes to rest, can be used to estimate the height or width of grain piles. Angle of repose depends on things like size and shape of kernels, moisture content, fines and foreign material content, presence of mold, and filling or emptying method, and can vary greatly. For example, the angle of repose for dry corn can range from 15 to 26 degrees. However, the standard angle of repose for healthy dry corn is 23 degrees.

Pre-experiment Checklist

Check that the following are available (and clean) before measuring bulk density:

- Seedburo seed hopper system (see diagram below)
- Mettler-Toledo bulk balance
- Lab scoop
- Biomass sample

Procedure

1. Pre-weigh density cup, labeled ½ L and record weight (W_{DC}) to the nearest 0.1g.
2. Tare (zero-out) balance.

3. Make sure slide gate is shut so that no material can flow out.
4. Fill filling hopper with biomass sample using lab scoop.
5. Place density cup, previously weighed, underneath filling hopper.
6. Open slide gate, fill density cup half full, and then close slide gate.
7. Take density cup and tap it on a solid surface three times from a height of approximately 1 inch.
8. Place density cup underneath funnel filling device, and again open slide gate, allowing the biomass container to overflow. Immediately close slide gate.
9. Tap density cup on a solid surface 3 times from a height of approximately 1 inch again to settle the material.
10. Use strike off stick to strike off overflow material so that material is flush with the top of density cup container.
11. Reweigh full density cup and record the weight (W_{DC+BM}).
12. Pour biomass back into filling hopper (slide gate is closed).
13. Tare (zero-out) balance.
14. Move funnel filling arm away so that filling hopper is directly above the lab bench.
15. Place a large Kim wipe/paper towels below lower funnel to create a flat surface below filling hopper.
16. Open slide gate and allow the material to freely flow out onto the flat surface. (Do not touch or disturb this pile of biomass.)
17. Move filling hopper back to its original position.
18. Measure the total diameter and height (highest point) of biomass pile with a ruler.
19. Record the diameter (d_1) and height (h_1) of biomass pile.
20. Repeat bulk density and angle of repose measurements for each biomass sample such that there are two sets of data (weights and pile dimensions) for each biomass sample recorded.
21. Pour biomass carefully back into the original bag.
22. Wipe out density cup and filling hopper with paper towel into the garbage container before measuring a different biomass sample.

Data Analysis

1. Calculate the bulk density of each mysterious biomass sample using biomass weight data (W_{BM}) the equation below:

$$\text{Bulk density} = \_\_\_\_\_\_ \frac{\text{g}}{500\ \text{mL}} * \frac{1\ \text{kg}}{1000\ \text{g}} * \frac{1\ \text{mL}}{1\ \text{cm}^3} * \frac{1{,}000{,}000\ \text{cm}^3}{1\ \text{m}^3} = \_\_\_\_\_\_\_ \frac{\text{kg}}{\text{m}^3}$$

2. Calculate the average bulk density value for each biomass sample.
3. Calculate the angle of repose for each biomass pile and record.
4. Calculate the average angle of repose for each biomass sample.
5. Feel texture of each biomass with bare hands and record observations in lab notebook. Discuss how biomass texture might this impact flow of the material through the hopper (handling) and the angle of repose?
6. What does the magnitude of the angle of repose indicate about the differences between the mysterious biomass samples? What implications does this geometry have for storage facility design?

Higher Heating Value (HHV)

Background

The Parr 6400 Isoperibol (constant temperature surroundings) Calorimeter is used to measure the heats of combustion, specifically higher heating value (HHV) in cal/g or MJ/kg. HHVs are measured by a substitution procedure in which the heat obtained from the sample is compared with the heat obtained from a standardizing material, in this case, solid benzoic acid. The sample is burned in a high-pressure (450 psi or 30 atm) oxygen atmosphere within a metal pressure vessel or "bomb." The energy released by the combustion is absorbed within the calorimeter and the resulting temperature change is recorded.

The calorimeter set-up includes three systems: the calorimeter itself, the oxygen flow system, and the pneumatic water rinse system. The calorimeter is made up of the touch-screen control panel on the front, the combustion chamber which holds the bomb vessel; a water-holding tank, heater and pump used to maintain constant temperature in the bomb jacket; and the inlet/outlet ports for the oxygen and pneumatic rinse systems. The bomb vessel has two pieces: the canister, which stays in the instrument, and the sample holder, which serves as the sealing lid of the canister and holds the ignition wire, charge electrodes, and a wire loop to hold the sample cup. A cotton string is used as a "wick" between the ignition wire and the sample cup. To cause combustion, a charge is sent through the ignition wire which ignites the cotton wick, which in turn ignites the sample. After the combustion reaction, excess oxygen and combustion product gases are vented out the back of the calorimeter into the rinse collection container. The bomb vessel is rinsed several times with pressurized water after each test.

Some samples that have low energy content, high moisture content or just do not burn completely benefit from the practice of "spiking," in which a small amount of a well-burning material such as mineral oil or alcohol are added to the samples to aid combustion. Since the mass and the heating value of the "spike" can be known, these can be subtracted from the energy content calculations for the sample. A mineral oil spike will be used with biomass samples in this procedure.

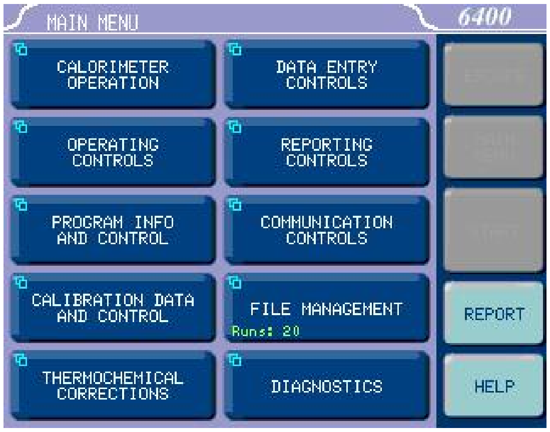
Pre-experiment Checklist

The following checklist is to be performed each time before starting a new analysis.

- Oxygen and air cylinders are open and set to the appropriate pressures: 450 psi for oxygen and 80 psi for air.
- Internal water-holding reservoir is full.
- External pressurized rinse tank has sufficient water.
- Sufficient clean sample cups and cotton strings are available.
- Printer is on and has paper.
- Benzoic acid standardization tablets and mineral oil are available.
- Instrument has been allowed to warm up. On the Calorimeter Operation submenu, toggle the Heater and Pump button to on. Wait for the jacket temperature to reach 30°C (10-20 minutes). Once the jacket water has warmed up, the bar on the bottom of the screen will become green and the Start Pretest button will be available (blue).
- Instructor has run an EE quality control test using benzoic acid.

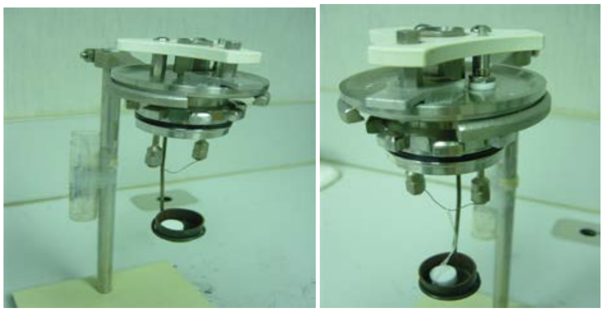
Procedure

1. On the Main Menu, press Calorimeter Operation button.

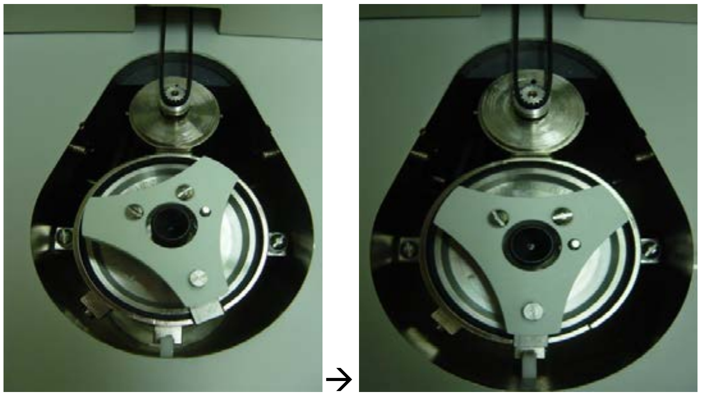


2. Make sure that the sample holder is locked into the bomb canister to seal the vessel and that the top lid is closed. Run a pretest (fill and rinse cycle) by pressing the Start Pretest button.
3. Place a clean (wiped out) metal sample cup on the balance and tare weight of the sample cup.
4. Add about 0.2 g herbaceous biomass or 0.4 g of woody biomass and record weight of sample.
5. Tare weight of sample cup and sample.
6. Add about 0.4 g of mineral oil using dropper (15-20 drops), trying to cover as much of the sample surface as possible. Record weight of spike.
7. Once instrument is in idle mode again, open lid and carefully remove sample holder by rotating counter-clockwise to unseal from bomb canister and lifting out.

8. Remove used sample cup if there is one, empty into sink, and wipe cup out with a Kim wipe.
9. Gently shake excess water off the sample holder over the sink and use a paper towel or Kim wipe to dry off the ignition wire (the rest of the assembly does not have to be dry). Place on sample holder stand.
10. Place full sample cup in sample holder.
11. Prepare a fresh cotton string "wick" by looping a piece of pre-cut cotton string around the ignition wire at the bottom of the V-shape, twisting the string around itself slightly, and placing the edges of the string on top of the sample. (The goal is to have the string connecting what will be the hottest part of the ignition wire to the sample so that the string will ignite and pass the flame down to the sample.)



12. Carefully lift the sample holder with the sample cup out of the stand and into the calorimeter, setting it into the bomb canister and rotating it clockwise until it seals into place.



13. Close the lid of the calorimeter.
14. On the Calorimeter Operation menu, make sure that Operating Mode reads Determination, then press the Start button.
15. A screen will ask if the current ID is to be used (Auto Sample ID Control is turned on, which means that the last digit of the sample ID will be increased by 1 for each subsequent test). If the auto-generate ID is acceptable, press Yes. If not, press no and enter a new sample ID, using Shift/Unshift button to toggle between letters and

numbers. IDs should be a group member's last name, followed by the number of the sample, followed by the number of the replicate. For example,

Ramierez 1 1 (Ramierez' first sample, first replicate)
Ramierez 1 2 (Ramierez' first sample, second replicate)

16. After entering a sample ID, enter sample weight (in grams) and press Enter.
17. For spike weight, enter weight of mineral oil added (in grams) and press Enter. This should start the analysis run.
18. Use the Calorimeter Operation screen to monitor the run. From this screen, the Temperature Graph button will display the bucket and jacket temperatures with time. The run is divided into Preperiod (oxygen pressurization), Time (firing) and Post period (combustion, temperature equilibration and measurement, rinse cycles) and lasts about 10 minutes. The instrument gives two sets of beeps during a run, one right before firing and one right before the first rinse cycles. ***Rinse cycles use pressurized water, so the venting process can be quite sudden and loud.***
19. To stop a run in progress, press the Abort button. Wait until the status in the Calorimeter Operation menu returns to Idle and the bar is green before opening the calorimeter. If there was a misfire (i.e. the wick fails to ignite), a misfire error message will be given.
20. After a run is complete and the status on the Calorimeter Operation menu returns to idle, open the calorimeter lid and carefully twist and lift off the sample holder.
21. Clean and rinse out sample cup.
22. Record HHV shown on printout in lab notebook.
23. Repeat test process so that at least two replicates have been done for each sample.

Data Analysis

1. Calculate the average volumetric energy density for each biomass using HHV and bulk density data:

Biomass #1 $\_\_\_\_\_\_\frac{\mathrm{MJ}}{\mathrm{kg}} * \_\_\_\_\_\frac{\mathrm{kg}}{\mathrm{m}^3} = \_\_\_\_\_\_\_\_\_\_\frac{\mathrm{MJ}}{\mathrm{m}^3} = \_\_\_\_\_\_\_\_\_\frac{\mathrm{GJ}}{\mathrm{m}^3}$

Biomass #2 $\_\_\_\_\_\_\frac{\mathrm{MJ}}{\mathrm{kg}} * \_\_\_\_\_\frac{\mathrm{kg}}{\mathrm{m}^3} = \_\_\_\_\_\_\_\_\_\_\frac{\mathrm{MJ}}{\mathrm{m}^3} = \_\_\_\_\_\_\_\_\_\frac{\mathrm{GJ}}{\mathrm{m}^3}$

2. Attempt to identify mysterious biomass samples based on all data collected using tables of known biomass property data.

Lab Procedure Part 2: Biomass Processing

Safety Checklist

- Proper attire is worn (long pants and closed-toe shoes).
- Food and drinks are stored and consumed outside the laboratory.
- Lab coat and safety glass are worn.
- Latex or nitrile gloves are used when handling samples and chemicals.

Problem Statement

Your team has been asked back into the "secret" biomass prep room by your BRL grinding operative. Located here are two sieve shakers and a knife mill for biomass processing. In order for biomass to be used as feedstock in fast pyrolysis and gasification reactors, the biomass particles must be an appropriate size; if the biomass particles are too big, the pyrolyzer heat requirements will increase and the yields will be lower. Your grinding operative has two biomass samples to prepare for the fast pyrolysis unit located on the 3rd floor. You will be sieving the biomass in the Ro-tap shakers to determine particle size distribution, separating the biomass into "too fine," "just right," and "needs grinding" piles, grinding the biomass in the knife mill, and finally, sieving the ground biomass to determine particle size distribution and to separate the sizes again. You will also monitor knife mill power consumption throughout the grinding process.

Particle Size Reduction

Background

Rot-tap sieve shakers use both rotational motion and a "tapping" bar to move biomass through sieves. The sieve shakers are controlled by timers to run for a specified time (typically 10-15 minutes) and speed dials for rotational frequency. Sieves with different screen mesh sizes are stacked with the largest screen on the top and the smallest screen on the bottom such that the finer biomass particles end up lower in the stack.

The Retsch knife mill reduces biomass particle size by "cutting" it through a screen of a specific size. The knife mill contains a hopper where the biomass is fed, a rotor housing where a 3-bladed rotor cuts biomass and a screen filters out larger particles, and a collection container, see Figures 1 and 2. The screen size is chosen based on the desired particle size; screens with openings ranging from 10 mm to 0.25 mm are available. *The knife mill is a powerful and potentially dangerous machine whose operation presents mechanical, heat, electrical, dust and noise hazards. Proper safety equipment must be worn at all times and the standard operating procedure must be followed.*

Power utilized to grind biomass is of interest because biomass preparation is often a significant portion of feedstock cost; these power costs can "make or break" the economics of a process. In this experiment, power consumption of the knife mill will be measured using a clamp-on amp meter, first while the rotor is empty to get a baseline and then while biomass is being fed through the rotor. Power (in units of Watts) is related to current (amps) by: power = current * voltage. If the voltage of the mill is known and the current can be measured, the power can be calculated.

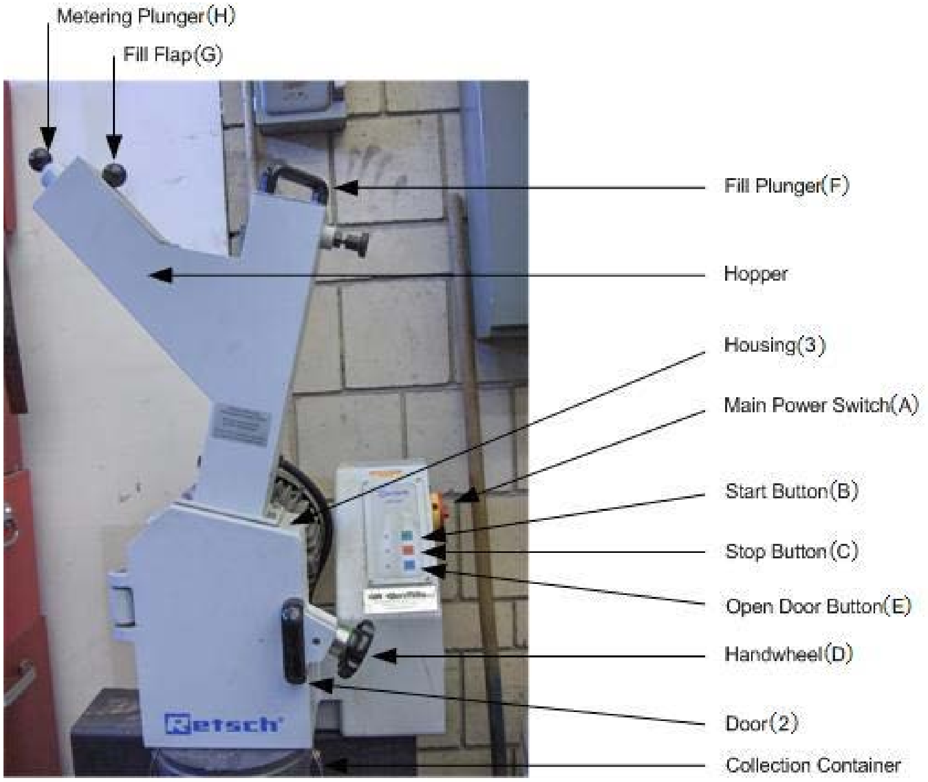


Figure 1. Components of the Retsch knife mill.

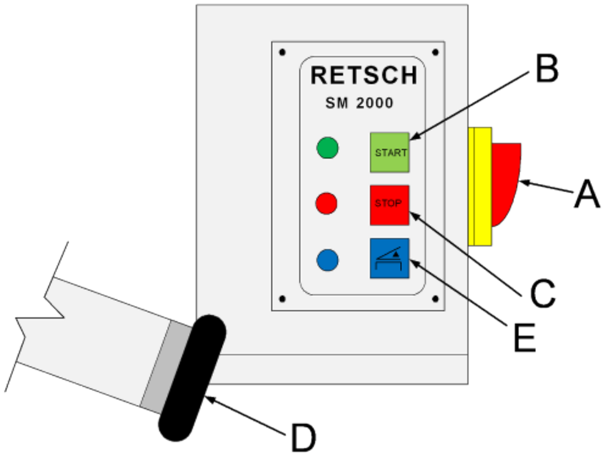


Figure 2. Knife mill control and safety components.

Pre-experiment Checklist

Check that the following are available (and clean) before beginning:

- Ro-tap sieve shakers
- sieves and bottom catch pan

- Retsch knife mill
- clamp-on amp meter
- biomass samples
- biomass scoop
- biomass buckets
- bulk balance
- shop vacuum (for clean-up)

Procedure

1. Select appropriate sieves including bottom catch pan and weigh each using the bulk balance.
2. Record the sieve pan mesh sizes (in microns) and empty weight of each pan.
3. Stack the sieves such that the catch pan is on the bottom and the sieves are ordered largest to smallest mesh size (top to bottom).
4. Place biomass in the top pan (largest screen mesh size) such that it is about half full and cover with lid.
5. Insert sieve stack onto Ro-tap shaker, making sure that tapping bar rests on lid.
6. Set rotation speed to desired frequency and shaker timer to 10-15 minutes. Shaker will start as soon as timer is set.
7. Once shaker has completed the cycle, remove sieve stack and reweigh each sieve full, including the bottom catch pan. Record the full weights of each.
8. Carefully empty biomass from sieves/pan into the appropriate buckets:
    a. <200 µm into "too fine" bucket
    b. 200-500 µm into "just right" bucket
    c. >500 µm into "needs grinding" bucket
9. Clean out sieves and bottom catch pan by tapping over a garbage can and wiping out with a dry paper towel.
10. Repeat steps 1-9 until enough material has been collected in the "needs grinding" bucket determined by your operative.
11. Record the size of the knife mill screen provided by your operative.
12. Measure the baseline current flowing to the knife mill using the clamp-on power meter. Record the baseline current in amps (A).
13. Grind biomass using Knife Mill Operation instructions below.
14. Have one person monitor current flowing to the knife mill. Record the time and current about every 30 seconds while rotor is on. A stopwatch is recommended.
15. Once grinding is complete, power down and clean up knife mill.
16. Determine particle size distribution of ground biomass by repeating steps 1-9.

Knife Mill Operation

1. Opening the grinder (Refer to Figures 1 and 2 for letter/number references)
    a. Plug grinder in and make sure motor has completely stopped.
    b. Turn main power switch **(A)** on. Wait until safety check is complete as indicated by LED lights C and E.
    c. Press Open door button **(E)**. LED E goes out; LED C stays lit. This unlocks the safety latch.

   d. Pull handwheel **(D)** out and turn **counterclockwise**.
   e. Open door **(2)**.
   f. Lift upper housing **(3)**.
   g. Make sure rotor housing is clean and proper screen is installed with the arrow on the screen pointing in the same direction as rotor movement (counter-clockwise).
2. Closing the grinder
   a. Lower the upper housing **(3)**.
   b. Make sure the mating surfaces are clear.
   c. Close door **(2)**.
   d. Pull handwheel **(D)** out and turn **clockwise**.
3. Loading the hopper

   The hopper must be loaded before the grinder is turned on. As the biomass is being ground, more biomass can be added to the hopper.

   a. Make sure fill plunger **(F)** is closed (down).
   b. Pull out metering plunger **(H)**.
   c. Open fill flap **(G)**.
   d. Load biomass.
   e. Close fill flap **(G)**.
   f. As hopper empties, more biomass may be loaded during operation.
4. Start-up
   a. Make sure fill plunger **(F)** is down before starting.
   b. Turn on main power switch (**A)**. Wait while safety check is complete indicated by LED lights C and E.
   c. Press Open door button **(E)**. LED E goes out and LED C lights.
   d. Pull handwheel **(D)** out and turn **counterclockwise** to open.
   e. Clean or change screens as needed.
   f. Pull handwheel **(D)** out and turn **clockwise** to close. LEDs E and C light.
5. Turning ON
   a. Press Start button **(B)** to start. LEDs C and E go out; LED B lights.
   b. Slowly pull fill plunger **(F)** up.
   c. When you hear the grinder begin to grind the biomass, keep bringing the fill plunger **(F)** up to allow remaining biomass to fall into rotor.
   d. Slowly lower fill plunger **(F)** onto biomass.
   e. If grinder sounds overwhelmed with biomass, lift fill plunger **(F)** up.
   f. Repeat steps c) and d) until the fill plunger can rest on the biomass during operation.
   g. Fill hopper as needed. See step 3.
6. Pausing and opening door
   a. Press Stop button **(C)**.
   b. Wait until rotor has stopped spinning as indicated by lit LED E and C.
      i. Press Open door button **(E)**. LED E goes out.
      ii. Pull handwheel **(D)** out and turn **counterclockwise** to open.
      iii. The door **(2)** and the housing **(3)** can now be opened if needed.
7. Closing door and resuming
   a. Shut door (**2)**.

    b. Pull handwheel (**D)** out and turn **clockwise** to close. LEDs E and C light.
    c. Press Start button (**B)** to resume.

8. Turning OFF
    a. Press Stop button **(C)**.
    b. Wait until rotor has stopped spinning as indicated by lit LED E.
    c. Turn off main power switch **(A)**.
    d. Remove all biomass from housing and collection container.
    e. Close Housing door.
    f. Unplug grinder and coil cord.
    g. Sweep/vacuum up dust on the ground and grinder.

Safety Notes

- Do not open hand-wheel **(D)** while running. This will damage mechanical components.
- Do not turn off main power switch **(A)** while running. This will lock the housing door **(2).**
- Do not attempt to open door without closing hand-wheel **(D).** The grinder cannot be started because the safety interlock has been broken. To avoid this, lock the door using hand-wheel **(D)**; turn off main power switch **(B);** turn on main power switch **(A).**

Data Analysis

1. Calculate the weight of biomass in each sieve by subtracting the empty weight from the full weight.
2. Organize the biomass particle size distribution data in a table and create a bar graph of the distribution for as-received and ground biomass.
3. Calculate the current at each time point in grinding by subtracting the baseline current from the measured current values.
4. Create a line graph of knife mill current over time. Label any interesting time points such as when blade was turned on, when biomass reached the blades and a steady-state power level.
5. Estimate the amount of power required to grind the biomass by multiplying the current data by the knife mill voltage and the amount of time the mill was running.
6. Compare particle size distributions and power requirements with the other group. Which biomass needed more work to be ready as a feedstock? Which biomass was easier to grind?

Tables of Known Biomass Properties

Biomass Composition, Chemical Characteristics and Physical Characeristics

N/A = not applicable

		COMPOSITION		
		cellulose (%)	hemi-cellulose (%)	lignin (%)
Bioenergy Feedstocks	corn stover	35	28	16-21
	sweet sorghum	27	25	11
	sugarcane bagasse	32-48	19-24	23-32
	sugarcane leaves			
	hardwood	45	30	20
	softwood	42	21	26
	hybrid poplar	42-56	18-25	21-23
	bamboo	41-49	24-28	24-26
	switchgrass	44-51	42-50?	13-20
	miscanthus	44	24	17
	Arundo donax	31	30	21
Liquid Biofuels	bioethanol	N/A	N/A	N/A
	biodiesel	N/A	N/A	N/A
Fossil Fuels	Coal (low rank; lignite/sub-bituminous)	N/A	N/A	N/A
	Coal (high rank; bituminous/anthracite)	N/A	N/A	N/A
	Oil (typical distillate)	N/A	N/A	N/A

		CHEMICAL CHARACTERISTICS				
		heating value (gross, unless specified; GJ/t)	ash (%)	sulfur (%)	potassium (%)	Ash melting temperature [some ash sintering observed] (C)
Bioenergy Feedstocks	corn stover	17.6	5.6			
	sweet sorghum	15.4	5.5			
	sugarcane bagasse	18.1	3.2-5.5	0.10-0.15	0.73-0.97	
	sugarcane leaves	17.4	7.7			
	hardwood	20.5	0.45	0.009	0.04	[900]
	softwood	19.6	0.3	0.01		
	hybrid poplar	19.0	0.5-1.5	0.03	0.3	1350
	bamboo	18.5-19.4	0.8-2.5	0.03-0.05	0.15-0.50	
	switchgrass	18.3	4.5-5.8	0.12		1016
	miscanthus	17.1-19.4	1.5-4.5	0.1	0.37-1.12	1090 [600]
	Arundo donax	17.1	5-6	0.07		
Liquid Biofuels	bioethanol	28		<0.01		N/A
	biodiesel	40	<0.02	<0.05	<0.0001	N/A
Fossil Fuels	Coal (low rank; lignite/sub-bituminous)	15-19	5-20	1.0-3.0	0.02-0.3	~1300
	Coal (high rank; bituminous/anthracite)	27-30	1-10	0.5-1.5	0.06-0.15	~1300
	Oil (typical distillate)	42-45	0.5-1.5	0.2-1.2		N/A

		PHYSICAL CHARACTERISTICS		
		Cellulose fiber length (mm)	Chopped density at harvest (kg/m^3)	Baled density [compacted bales] (kg/m^3)
Bioenergy Feedstocks	corn stover	1.5		
	sweet sorghum			
	sugarcane bagasse	1.7	50-75	
	sugarcane leaves		25-40	
	hardwood	1.2		
	softwood			
	hybrid poplar	1-1.4	150 (chips)	
	bamboo	1.5-3.2		
	switchgrass		108	105-133
	miscanthus		70-100	130-150 [300]
	Arundo donax	1.2		
(typical bulk densities or range given below)				
Liquid Biofuels	bioethanol	N/A	N/A	790
	biodiesel	N/A	N/A	875
Fossil Fuels	Coal (low rank; lignite/sub-bituminous)	N/A	N/A	700
	Coal (high rank; bituminous/anthracite)	N/A	N/A	850
	Oil (typical distillate)	N/A	N/A	700-900

The U.S. Department of Energy's Energy Efficiency & Renewable Energy Biomass Energy Program
http://www1.eere.energy.gov/biomass/

Thermochemical Properties of Biomass
see Table 3.3 on page 67 in *Biorenewable Resources: Engineering New Products from Agriculture.*

Density and Volumetric Energy Content of Fuels
see Table 3.5 on page 69 in *Biorenewable Resources: Engineering New Products from Agriculture.*

Volumetric Energy Density

Definition: amount of energy (KJ, cal, BTU) in a certain volume (m^3, L, gal) for a given material.

Gasoline $48{,}200\frac{kJ}{kg} * 740\frac{kg}{m^3} = 35{,}700{,}000\frac{kJ}{m^3} = 35.7\frac{GJ}{m^3}$

Coal $33{,}800\frac{kJ}{kg} * 650\frac{kg}{m^3} = 22{,}000{,}000\frac{kJ}{m^3} = 22.0\frac{GJ}{m^3}$

Biodiesel $39{,}600\frac{kJ}{kg} * 900\frac{kg}{m^3} = 35{,}600{,}000\frac{kJ}{m^3} = 35.6\frac{GJ}{m^3}$

Ethanol $29{,}700\frac{kJ}{kg} * 790\frac{kg}{m^3} = 23{,}500{,}000\frac{kJ}{m^3} = 23.5\frac{GJ}{m^3}$

Biomass #1 $\underline{\qquad\quad}\frac{kJ}{kg} * \underline{\qquad}\frac{kg}{m^3} = \underline{\qquad\qquad\quad}\frac{kJ}{m^3} = \underline{\qquad\qquad}\frac{GJ}{m^3}$

Biomass #2 $\underline{\qquad\quad}\frac{kJ}{kg} * \underline{\qquad}\frac{kg}{m^3} = \underline{\qquad\qquad\quad}\frac{kJ}{m^3} = \underline{\qquad\qquad}\frac{GJ}{m^3}$

How many gallons of alternative energy products are required to equal 1 gal of gasoline?

Coal $1\ gal\ gasoline * \frac{35.7\ {}^{GJ}/_{m^3}\ gasoline}{22.0\,{}^{GJ}/_{m^3}\ coal} = 1.62\ gal\ coal$

Biodiesel $1\ gal\ gasoline * \frac{35.7\ {}^{GJ}/_{m^3}\ gasoline}{35.6\,{}^{GJ}/_{m^3}\ biodiesel} = 1.003\ gal\ biodiesel$

Ethanol $1\ gal\ gasoline * \frac{35.7\ {}^{GJ}/_{m^3}\ gasoline}{23.5\,{}^{GJ}/_{m^3}\ ethanol} = 1.52\ gal\ ethanol$

Biomass #1 $1\ gal\ gasoline * \frac{35.7\ {}^{GJ}/_{m^3}\ gasoline}{\underline{\qquad}\,{}^{GJ}/_{m^3}\ biomass} = \underline{\qquad\quad}\ gal\ biomass$

Biomass #2 $1\ gal\ gasoline * \frac{35.7\ {}^{GJ}/_{m^3}\ gasoline}{\underline{\qquad}\,{}^{GJ}/_{m^3}\ biomass} = \underline{\qquad\quad}\ gal\ biomass$

Calculating Bulk Density

Biomass #1

$$\_\_\_\_\_\_\frac{g}{500\ mL} * \frac{1\ kg}{1000\ g} * \frac{1\ mL}{1\ cm^3} * \frac{1{,}000{,}000\ cm^3}{1\ m^3} = \_\_\_\_\_\_\frac{kg}{m^3}$$

Biomass #2

$$\_\_\_\_\_\_\frac{g}{500\ mL} * \frac{1\ kg}{1000\ g} * \frac{1\ mL}{1\ cm^3} * \frac{1{,}000{,}000\ cm^3}{1\ m^3} = \_\_\_\_\_\_\frac{kg}{m^3}$$