Environmental Health and Safety (EH&S)
2809 Daley Drive
Ames, IA 50011-3660
Phone: 515 294-5359
Fax: 515 294-9357
www.ehs.iastate.edu

Standard Operating Procedure

Procedure: Measuring higher heating value (HHV) of biomass or char by Parr 6400 oxygen bomb calorimeter

Department: Biorenewable Resources & Technology

Building/ Room Number: Biorenewables Research Laboratory (BRL) 1114

Supervisor: Jacqulyn Baughman

Procedure Overview: Pre-weighed samples of biomass or char (as received condition) are burned completely in a sealed combustion chamber containing 30 atmospheres of pure oxygen. The heating value of the material is determined by the temperature increase in the surrounding water jacket. Heating values are standardized against benzoic acid. Samples are ignited using an electrically charged wire and a cotton string "wick." The sample chamber is flushed and cooled with water after each run.

Health and safety information for materials used: Compressed air and oxygen are under high pressure and will accelerate a fire; tanks should be separated from flammable gases and fires. Ground biomass and char can be fine powders and may cause dust hazards.

Hazard Control Measures:

- safety glasses
- dust mask (for handling fine powders)

Waste Disposal Procedures: Biomass, chars and any ash or unburned residue can be put into regular, non-hazardous garbage. As biomass and chars are very low in acid-forming N and S, the rinse water collection vessel can be emptied into the sink.

Decontamination Procedures: none

Spill containment and clean up procedures: Biomass, char and bed ash can be swept up or wiped up with a wet cloth and disposed of in the garbage.

Using substances requiring special procedures? No

Written By: Catherine Brewer **Date:** 5/18/11

Approved By: **Date:**

Detailed procedures, instrument operation and maintenance, emergency contact information and a list of those trained for this procedure are attached.

Equipment Description

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. This method is especially suitable for materials that have low energy contents. A representative 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; several electronic hook-ups for printers, networks, etc., 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, the charge electrodes for the ignition wire, and a wire loop on which the sample cups are placed. A cotton string is used as a "wick" between the ignition wire and the sample cup. The oxygen used to pressurize the bomb flows from a compressed cylinder, through a regulator and filter, and into the instrument through the back. 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 water after each test using air pressure to move the water through the system. The air flows from a compressed cylinder, through a regulator and into the metal rinse tank (sitting on the floor underneath the instrument). During a rinse, pressurized water flows from the rinse tank, into the rinse water port on the back of the instrument, through a small tube into the top of the bomb vessel, out a valve in the bottom of the bomb vessel, out the exhaust port in the back of the instrument and into the rinse collection container (also sitting on the floor underneath the instrument).

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. In the case of biomass, a spike is not likely to be necessary unless the sample is particularly fine or wet. In the case of chars, a spike should be used for two reasons: first to "wet down" the fine powder to prevent elutriation, and second, to moderate the rate of the burn (chars tend to have high energy values, small particles sizes and very low moisture contents which can lead to them burning too hot and too fast). Mineral oil will be the material used as a spike in this procedure.

Pre-Analysis Checklist

The following checklist is to be performed each time before turning on the calorimeter.

- Compressed oxygen and air tanks are hooked up to the instrument and have sufficient pressure for the tests: >500 psi for oxygen and >100 psi for the air.
- Internal water-holding reservoir is full. This is checked by removing the red plastic cover on the tank fill opening on the lower left of the back of the instrument. Water should be just visible in the bottom of the tank fill inlet. If more water is needed, add distilled water.
- External pressurized rinse tank has sufficient water. To check this, the tank has to first be depressurized. Make sure air cylinder is closed (so that air is no longer flowing from the cylinder to the rinse tank) and then open the black vent valve on rinse tank by moving it to the upright position. Wait until the air has stopped venting, then open the rinse tank by lifting up on the handle holding the lid in place. To remove the lid, lower it slightly and twist to maneuver out of the tank. If tank is less than half full, fill with distilled water. Replace lid and lock down handle to make sure it is sealed. Close black vent valve.
- Sufficient clean sample cups and cotton strings are available.
- Printer has paper.
- Benzoic acid standardization tablets and mineral oil are available.

Instrument Warm-up

1. Make sure oxygen and air cylinders are open and set to the appropriate pressures: 450 psi for oxygen and 80 psi for air (gas cylinders should be opened and closed using the main valves rather than the dial on the regulators which are already set to the correct pressure).
2. Turn on printer (switch on right side).
3. Turn on instrument (switch on back of instrument) and wait for screen to load to main menu.
4. 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).
5. 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.
6. Once pretest is finished, run an EE quality control check (see page 5).

Instrument Operation

1. If instrument has been idle for more than 15 minutes, run another pretest cycle to condition instrument (you can weigh out samples while this is running—steps 2-4).
2. Place a clean (wiped out) metal sample cup on the balance and tare weight of the sample cup.
3. Add about 0.2 g herbaceous biomass or 0.4 g of woody biomass or 0.4 g of char and record weight of sample.
4. If a spike is needed, tare weight of sample cup and sample. 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.
5. 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.

6. Remove used sample cup if there is one, empty into sink, and wipe cup out with a Kim wipe.
7. 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.
8. Place full sample cup in sample holder.
9. 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.)
10. 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.
11. Close the lid of the calorimeter.
12. On the Calorimeter Operation menu, make sure that Operating Mode reads Determination, then press the Start button.
13. 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 descriptive, unique (using the same sample ID will overwrite any data for that sample in the memory) and end in a number that indicates the number of replicates that have been run. For example,
    a. BA1216101 would be a benzoic acid calibration check run on Dec ember 16, 2010, the first replicate.
    b. bamboochar4002 would be bamboo char made at 400°C, the second replicate.
14. After entering a sample ID, enter sample weight (in grams) and press Enter.
15. For spike weight, enter weight of mineral oil added (in grams), or if not using mineral oil, type in 0 and press Enter. This should start the analysis run.
16. Use the Calorimeter Operation screen if you want 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/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.***
17. 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. In general, the run can simply be restarted and the misfire noted in case there are any unusual results.
18. 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. Inspect the sample holder and the inside of the canister for residue. There will often be some ash materials remaining in the sample cup, but residue in other places can signal a spill out of the cup during combustion or

elutriation of burning powders. If the results from the run seem low, repeat the test to verify complete combustion. If a burnt rubber smell is present, check the O-ring seals at the top of the canister and on the sample holder for damage and replace if necessary.

19. Repeat test process for next sample.

Instrument Shutdown

1. Make sure that used sample cup has been removed for cleaning and the empty sample holder replaced inside the instrument. Close the calorimeter lid.
2. On the Main Menu, press the power button and confirm system shutdown. The screen will inform the user when it is safe to switch off the instrument.
3. Turn off the instrument (back panel).
4. Turn off the printer (right side).
5. Close the gas cylinders by using the main valve (not the dial on the regulator).
6. Clean all sample cups, return supplies to draw, clean balance and surrounding area, cap and put away mineral oil and benzoic acid containers, and remove printed tape from printer.

Instrument Calibration

Two standardized values are used in each run, the energy equivalent (EE) factor and the spike HHV. The EE factor is the energy correction value that accounts for heat absorbed by the calorimeter during the combustion and is typically 920-940 cal/°C for this instrument. This is determined by averaging the energy corrections for 10 runs of the benzoic acid standard. Values for all past standardization runs are stored in the memory and only the most recent 10 are used to automatically calculate EE. The instrument should be recalibrated if there are any changes to the components (i.e. a different bomb vessel is installed) or if a quality control run of benzoic acid is outside the acceptable deviation.

To do an EE quality control check:

1. Do one or more measurements of the benzoic acid under Determination mode.
2. Compare the average HHV to values in Tables 6-1 (J/g) or 6-2 (cal/g) on pages 62-63 of the operation manual. If the average deviates from the listed value less than the maximum permissible deviation, the instrument does not need to be recalibrated.
    a. For example, the average of two runs of benzoic acid tablets gives a heat of combustion of 26.504 MJ/kg (26504 J/g). The accepted value for benzoic acid is 26454 J/g, meaning the deviation was 50 J/g. In row 2, column 4 of Table 6-1, the maximum permissible deviation for the average of 2 observations is 56.1 J/g. Since 50 < 56.1, the instrument is measuring within the acceptable deviation and does not need to be recalibrated.
3. If the average deviates more than the permissible deviation, more observations may be taken (especially if only one observation was used the first time). Otherwise, the instrument needs to be calibrated.

To calibrate the EE value:

1. Use the same procedure as when doing a quality control check exception that the Operating Mode button on the Calorimeter Operation menu must be toggled to Standardization (instead of Determination).
2. After 10 standardization runs are completed successfully, go to Calibration Data and Controls Menu and open the Bomb 1 sub-menu which will list the current EE value, # runs, EE relative standard deviation and bomb fire count.
3. Press the Update Statistics button.
4. Compare the new EE value to the old value and check the relative standard deviation. If the values are significantly different or if the standard deviation is higher than ~0.2%, use the Report button on the right side to access the data menus for the standardization runs. Check for any outliers (i.e. misfires, incomplete burns, etc.); delete those files and repeat those tests.
5. Record the date and the new EE value.

To calibrate spike HHV:
If a different spike or a new bottle of mineral oil is to be used for the spike, the spike HHV must be calibrated. This is done by running 10 samples of the same amount of spike and obtaining an average heat of combustion. Once this value is obtained, it must be entered on Operating Controls Menu, under Spike Controls then Heat of Combustion of Spike.

Maintenance
Occasionally, the ignition wire will break and need to be replaced (every 50-100 runs). Do this by loosening the two screws holding the wire in place, discarding the pieces of old wire and cutting a new 2" (4-6 cm) piece of wire from the maintenance kit. Bend the wire into a slight V-shape and attach to the holder by placing an end under the screw such the tightening the screw causes the wire to wrap around it. The wire "V" should be about ½-1" (2-3 cm) deep (i.e. making a V but not too close to the sample cup holder).
When replacing the wire, also check the electrode contact pins on the sample holder and on the lid of the calorimeter for build-up. Remove any residue from the ends with a mild abrasive such as a pencil eraser.

Approximately every 500 runs , the O-rings and seals on sample holder, inside the vessel and elsewhere in the calorimeter need to be replaced. The instrument is currently set to give a notification after 500 firings. Extra O-rings and seals are located in the maintenance kit. Instructions and part numbers can be found in Chapter 9 of the operation manual; pictures are available on the presentation on the thumb drive stored with the operation manual. *Do not use metals tools to remove O-rings and seals from seal grooves as these can scratch the surfaces making it more difficult to maintain a good seal*. Instead, push O-ring away from seal groove using a pinching motion with one's fingers and then remove the O-ring by either sliding it off or cutting it.

The oxygen and air gas cylinders are leased from the ISU Chemistry Stores and must be returned as soon as possible after all usable pressure has been utilized. New air tanks can be picked up from Chemistry Stores whenever it is opened, but the high purity oxygen tanks must be ordered (1-2 week lead time).

Used tanks should be closed, the In Use portion of the tag removed (so that it reads Empty), and the tanks taken to the outdoor cylinder rack behind the building near the dumpster.

Chemistry Stores Counter/Orders: (515) 29**4-0203** Office/Accounts: (515) 29**4-4413**

Emergency Contacts

Jacqulyn Baughman
Lab Coordinator/Supervisor
Office: (515) 294-9451 Cell: (414) 460-5776

Catie Brewer
Graduate Research Assistant
Cell: (206) 290-1234

Marjorie Rover
Lab Manager
Office: (515) 29**4-2984** Cell: (319) 230-1163 Home: (515) 292-3671

Ryan Smith
BEI Program Coordinator
Office: (515) 29**4-6244** Cell: (515) 203-1640 Home: (719) 660-2262

Dr. Robert Brown
BEI/CSET Director
Office: (515) 29**4-7934** Cell: (515) 520-1337 Home (515) 460-3434

Approved Trainers:
Jacqulyn Baughman, Catie Brewer, Marge Rover

Training Sign-Off

Trainee	Date	Trainer