ANALYSIS OF PCS BIOFUEL FROM ANAEROBIC DIGESTION RESIDUALS

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Analysis of PCS Biofuel Produced from Anaerobic Digestion Digestate.

Determination of Higher Heating Value and Proximate Analysis PCS Biofuel produced from Anaerobic Digestion digestate feedstocks.

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INTRODUCTION:

Samples of wet digestate from an anaerobic digestion process were presented to this laboratory for conversion to PCS Biofuel for analysis on December 6, 2018. The samples were received in a wet state and were processed to a biofuel as received without drying. The higher heating value (HHV) was determined by bomb calorimetry using a Parr 6200 Bomb Calorimeter. The Proximate analysis was determined via Thermogravimetric analysis using a Mettler TGA/DSC1 using a modified ASTM E1171 method. The Thermal behavior was determined by thermogravimetric analysis using a Mettler TGA/DSC1. The soluble components in the catalyst solution were analyzed using a Thermo ISQ GC/MS.

The results indicate that the biomass is easily transformed into an excellent high energy density coal replacement The Higher heating value was similar to a high-quality coal being on the order of 29.5 GJ/Tonne or about 12,700 BTU/lb.

The proximate analysis shows the material had relatively low ash of 3% while the Fixed Carbon was 36.2% and volatiles were 59.6%

RESULTS

MOISTURE CONTENT

The as-received samples were processed "as is". The feedstock was rather in homogeneous having the consistency of a thick stew with large chunks of wood in it. Using the data from the Biofuel processing we estimate the average moisture content was 70% $\pm$ 5%

CONVERSION OF A/D DIGESTATE TO PCS BIOFUEL

As received samples of 195.58 grams of anaerobic digestion digestate were placed in a glass liner and the dilute catalyst solution was poured over the feedstock so that it was covered. The liner was placed in the reactor and the reactor was sealed. The reactor was placed in a heating mantle and heated to 240°C and then held at temperature was held at 240°C for 1 hour, the reactor was then allowed to cool via ambient convection to room temperature. Once the reactor had cooled to room temperature it was opened and the sample separated from the catalyst solution. The biofuel was washed with tap water and dried in an over at 70°C for 48 hours prior to further testing. After drying 38.92 grams of biofuel was recovered.

HIGHER HEATING VALUE

Oxygen Bomb Calorimeter to determine HHV

To determine the gross or higher heating value (HHV) of a fuel using a bomb calorimeter the sample to be tested is placed inside a pressure vessel, called a bomb. The bomb is then sealed and compressed oxygen is added into the bomb. The fuel inside the bomb is ignited and the resulting temperature rise is used to determine the heating value of the fuel.

Parr 6200 Isoperibol Oxygen Bomb Calorimeter as per ASTM D5865

The Parr 6200 bomb calorimeter uses an Isoperibol design. That is, the test bomb and water bucket are held in constant temperature environment. This allows the heat flow losses from the bucket to the environment to be constant and known. This design contrasts with the zero-heat loss design where the outside temperature varies to follow the bomb's temperature increase. (1)

The bomb calorimetry tests were conducted as per the ASTM D5865: "Standard test method for gross calorific value of coal and coke." The operation of the Parr 6200 calorimeter was as is outlined in the Parr manual. The higher heating values (HHV) for the feedstock and product are presented in table 1 below.

PROXIMATE ANALYSIS

Thermogravimetric Analysis is a method of analysis that determines the mass loss of a material as it is heated as a predetermined rate in a controlled atmosphere. The primary measurement is mass loss which is often reported as a percentage of initial weight.

Using a reference crucible and a sample crucible where the temperature of the reference and sample can be determined in a controlled atmosphere analysis technique can be extended to measure heat flow. This method is known as Differential Scanning Analysis or DSC. The heat flow is a determined quantity derived from the difference between the reference and sample temperatures as a sample is heated. (3)

Mettler TGA/DSC 1 Thermogravimetric Analyzer & Differential Scanning Calorimeter.

The Mettler TGA/DSC1 is a high-resolution microbalance that features microgram resolution over the whole temperature range from room temperature to 1100°C. (4) In addition to measuring the mass loss as a function of temperature it can also measure the heat flow using DSC heat flow measurements simultaneously while measuring mass loss. The oven cell is gas tight to control the atmosphere the samples are subjected to. The TGA/DSC1 has a horizontal oven design to minimize turbulence from thermal buoyancy and purge gas flow.

The unit is equipped with a DTA sensor that measures the temperature of the sample and a reference crucible. The DTA sensor allows the heat flow to be measured at the same time as the mass loss is being determined. A 70ul alumina crucible was used for the experiments in this project. For more information please see Wagner(2009) [5]

The Mettler TGA/DSC1's balance has a mass range of 1g is accurate to 1ug. It has a weighing accuracy of 0.005% and a weighing precision of 0.0025%. The furnace is capable of a heating rate of 150°C per minute and the maximum temperature of 1100°C. The sensor used is the DTA unit with dual platinum pans with temperature sensors attached. (4)

The isothermal accuracy of the balance was measured to be 0.9ug while the measured drift upon heating from 50°C to 1100°C was measured to be 231.7ug at the factory prior to delivery. DTA signal accuracy was measured at 150°C under isothermal conditions the balance error was determined to be 1.12ug while the heat flow was measured to be 0.046 mWpp. (4)

Prior to use the unit was calibrated using the melting point of indium and zinc as per the standard method recommended by the manufacturer.

Proximate analysis by TGA. ASTM E1131

The ASTM E1131 is the standard Test Method for Compositional Analysis by Thermogravimetry. ASTM E1131 provides a general technique incorporating thermogravimetry to determine the amount of highly volatile matter (moisture), medium volatile matter, combustible material, and ash content of compounds. (5) The proximate analysis is a standard for the measurement of the key physical parameter of a coal or coal like material.

The highly volatile matter includes moisture, low boiling point compounds and residual solvents that are in the material being tested. It includes all materials with a boiling point below 200°C. The medium volatile matter (usually noted as volatiles) is the material that volatizes or degrades between 200°C and 900°C. The combustible matter (fixed carbon in the case of coal or biofuel), is the material that oxidizes when the atmosphere is switched to an air or oxygen atmosphere. Finally, the ash is the residual matter left after all the combustible material has been lost. (5)

The method described in the ASTM E1131 has been modified somewhat to suit the thermogravimetric unit used. The thermal program used in this research is as follows:

- Step 1. Hold sample in nitrogen atmosphere for 5 minutes at 30°C. The flow rate of N_2 is 50ml/min.
- Step 2. Heat sample from 30°C to 900°C under a 50ml/min N_2 flow. Heating rate 10°C/min
- Step 3. Hold sample under N_2 flow of 50ml/min for 10 minutes at 900°C
- Step 4. Switch atmosphere to air with a flow of 50ml/min. hold temperature at 900°C.
- Finally, cool sample back to 30°C under an air flow of 50ml/min

The results are then calculated from the temperature vs. mass loss curve where the first mass loss centered on 100°C is noted as moisture, the mass loss on heating to 900°C under N_2 is calculated to be the volatile component of the biofuel. The mass loss upon switching to air atmosphere is calculated as the Fixed Carbon while the remaining material after combustion is denoted as ash. For the calculations, we use a horizontal step function in the Mettler TGA software.

The Higher Heating Value (HHV) and the Proximate Analysis for the samples are summarized in the table 1 below.

Table 1 Higher Heating Value and Proximate Analysis

Sample	HHV MJ/kg	Moisture %	Volatiles %	Fixed %	Ash %
PCS Biofuel produced from A/D Digestate	29.52	1.2	59.6	36.2	3.0

REFERENCES

1. **Parr Instrument Company.** *6200 Instruction Manual.* Moline, Illinois : Parr Instrument Company, 2010.

2. **Scott, R.** *"Physical Chemistry Resources," in Book 5 Thermo Analysis.* 2000.

3. **Wagner, M.** *Thermal Analysis in Practice: Collected Applications.* Schwerenbach : Metler Toledo, 2009.

4. **Mettler Toledo.** *TGA/DSC1 Star System Operating Instructions.* Schwerzenbach : Mettler Toledo, 2010.

5. **ASTM.** *ASTM E1131 Standard Test Method forCompositional Analysis by Thermogravimetry.* New York : ASTM, 2003.

Appendix 1. Mass loss as function of temperature for sample of PCS biofuel produced from A/D digestate.