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Measuring the heat of combustion of carbon-rich-compounds prepared by hydrothermal carbonization of different food substances using a home-made calorimeter.

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Abstract

It was possible to measure the heat of combustion of carbon-rich-compounds obtained by hydrothermal carbonization using a home-made calorimeter. It was necessary to use an oxidizer such as KNO_3 to enable uniform, complete and reproducible burning of the CRC. The heat lost by the calorimeter to the surroundings was calculated by measuring the heat of combustion of magnesium metal whose value was available from the literature. The correction factor accounted for both the weight fraction of the CRC in the burn mixture and the heat lost to the surroundings. Using the calorimeter constant, the heat of combustion of various components of biomass were calculated and found to agree reasonably well with previously reported values.

Introduction

Hydrothermal carbonization (HTC) is a wet pyrolysis process by which biomass feedstock is converted into solid carbon-rich-compounds (CRC) by heating with water in a pressurized atmosphere. Neither the biomass, nor the CRC product needs to be dried prior to, and after processing respectively. The CRC product is filtered and pressed into suitably sized shapes amenable for use as fuel. A carbon content of > 60% can be consistently obtained using HTC (1). HTC converts carbohydrates and carbon containing biomass into CRC products by a variety of simultaneously occurring chemical reactions such as demethanation, dehydration and decarboxylation; that may in turn be followed by condensation reactions yielding soluble polymeric CRC products (2). The type of reactions occurring depend on the nature of feedstock and the processing conditions (temperature, pressure and time) (3). The present study was performed to determine if a home-made calorimeter could be used to determine the heat of combustion of CRC manufactured by HTC.

Materials and methods

Sucrose, lot 217688, activated charcoal, Darco G60 grade, lot 193387, starch, lot 188191 lab grade and magnesium metal ribbon lot 174522 were obtained from Flinn Scientific, Batavia, IL. Potassium nitrate was procured from the local Lowes store as Spectracide™ stump remover granules, lot 02116-B, United Industries Corp., St. Louis, MO. The CRC was obtained from hydrothermal carbonization of different locally obtained food substances using a procedure that will be described in a future manuscript. City water direct from faucet was used for the study. The water used in the calorimeter was weighed on a Flinn Scientific

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balance, model 0B2141, d=0.01 g. The other chemicals were weighed on an Ohaus Pioneer balance, model PA153, d= 0.001 g, Ohaus Corp., Parsippany, NJ.

The calorimeter was built from two canned food cans. The outer larger can served to contain and direct the heat released from the burning carbon-rich-compound (CRC) to the inner can (11 cm tall, 7.5 cm dimeter) filled with 50 g of water. For this purpose, its top and bottom was opened with a can opener and 16 holes were drilled with a 3/16th drill bit, 1-2cm from the base of the outer can so as to supply enough oxygen to sustain the combustion of the CRC. The inner can was suspended 5 cm above the base of the outer can by drilling two diametrically opposite holes in the inner and outer can approximately 5 cm from the top and attaching the two with a rope knotted around the outer can (see figure 1a and figure 1b). The CRC was mixed with potassium nitrate in a mortar and pestle in a weight ratio of 1:0.6 and placed on an aluminum foil that in turn was placed on a porcelain crucible lid on the laboratory table. The porcelain crucible lid stayed horizontal to the surface by using 'children's molding compound' as a support.

Figure 1a

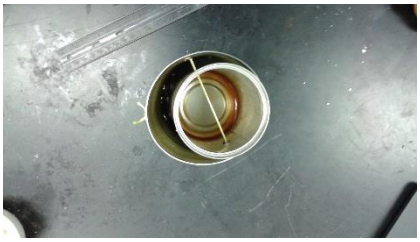

Figure 1b

Figure 1c

Figures 1a through 1d show the top and side views of the calorimeter, and the top and side views of the CRC sample holder respectively.

Figure 1d

The dried CRC was mixed with KNO_3in a weight ratio of 1.0: 0.6 and triturated in a ceramic mortar and pestle for 1 minute. This procedure ensured thorough mixing of the two components and a uniform particle size for all mixtures tested. The oxidizer, KNO_3 was mixed with the fuel CRC because it was found that it ensured that the CRC continued to burn when the source of ignition was removed, and that no part of the sample was left unburnt. The ratio of 1.0 to 0.6 parts by weight of CRC to KNO_3 was empirically determined to produce the most consistent and replicable burning in preliminary trials. A precisely weighed sample of this mixture (as near to 0.5 g as possible) was then placed on the aluminum foil on the porcelain crucible lid and ignited with a match. Once lit, the calorimeter was immediately placed above the crucible lid. The temperature of the water, precise to ± 0.1^oC, was measured using a Vernier temperature probe connected to a Vernier lab quest mini. Vernier logger lite™ 1.8.1, Vernier software and technology, Beaverton, OR was used to acquire and process the data. The maximum temperature of the water was recorded.

All CRC combustion experiments were performed in duplicate. The results reported are the mean and the percent relative standard deviation (RSD). No attempt was made to quantitate the amount of water present in the hydrothermalized CRC after drying for > 8 hours at 50^oC in a hot air oven (Quincy labs INC, Chicago, IL, model 10GC).

The heat of combustion of the CRC was calculated using the equation

$$Q = [m_w \times s \times \Delta t]/m_{crc} \qquad \text{Equation 1}$$

Where, Q is the heat of combustion in $J.g^{-1}$of the CRC, m_w is the mass of the water in g, s is the specific heat of water in $J.g^{-1}.\ ^oC^{-1}$, Δt is the difference in temperature of the water after and before being subjected to heat from the CRC and m_{crc} is the mass of the CRC in g. The specific heat of water was taken as 4.18 $J.g^{-1}.\ ^oC^{-1}$.

Due to the rudimentary design of the calorimeter, it lost heat to the surroundings. A calorimeter constant was needed that would normalize the heat of combustion obtained for a well-defined material to a literature value. For this purpose, experiments were performed using various materials. Activated charcoal as well as powdered barbeque briquettes were initially used for trial runs but neither burnt completely or consistently with the desired range of ratios with KNO_3. Sucrose and KNO_3 were mixed in ratios ranging from 0.28 to 0.53 (expressed as ratio by weight of sucrose to total weight of mixture). However, the burning of these mixtures was also found to be erratic and non-reproducible. Various weights of magnesium ribbon were thus utilized as a standard to calculate the heat lost by the calorimeter to the surroundings. The magnesium did not burn completely as well but that factor could be corrected for by weighing the unburnt magnesium ribbon after the experiment (see below).

Results and discussion

Table 1 shows the heat of combustion of the magnesium ribbon for different weights. Different weights were used to ascertain that the heat of combustion was independent of the weight of Mg used. The average value of the heat of combustion was 7595.58 J/g with a relative standard deviation (RSD) of 10.3%. Not all the magnesium weighed was found to

be burned, probably because of the limited oxygen and the relatively colder temperature of the sample holder into which it was placed as soon as it ignited. The unburnt pieces were weighed again after the experiment and the weight of the magnesium burnt was calculated (see table 1). A literature value of 630 KJ/mole (25.9 KJ/g) was used for the heat of combustion of magnesium (4).

Table 1: Calculation of the heat lost to the surroundings by the calorimeter by using magnesium

Weight of magnesium ribbon (g) – weight of unburnt magnesium ribbon (g) = weight of burnt magnesium (g)	Initial water temperature (^oC)	Maximum water temperature (^oC)	Heat of combustion (J/g)
0.240-.068=.172	16.0	21.6	6811.16
0.152-.024=.128	14.7	19.2	7354.69
0.261-.079=.182	14.6	22.1	8620.88

Weight of water= 50 g

This calorimeter constant was 25900 J/g / 7598.58 J/g = 3.41. The calorimeter constant corrects for the heat of combustion of the CRC by accounting for the heat loss to the surroundings. The heat of combustion of the CRC/KNO_3 mixture represents a CRC weight fraction of 0.625. Hence, all the values for the CRC heat of combustion reported have been multiplied by the calorimeter constant times the inverse of the CRC weight fraction, i.e. 3.41/0.625 = 5.46.

A representative CRC run (from apples, trial 2) is shown in Figure 2. The average time for the increase and subsequent stabilization of the water temperature from the heat generated by the CRC was typically of the order of 200 seconds.

Figure 2: A representative plot showing the increase in water temperature due to the heat liberated by the burning of the CRC and oxidizer mixture.

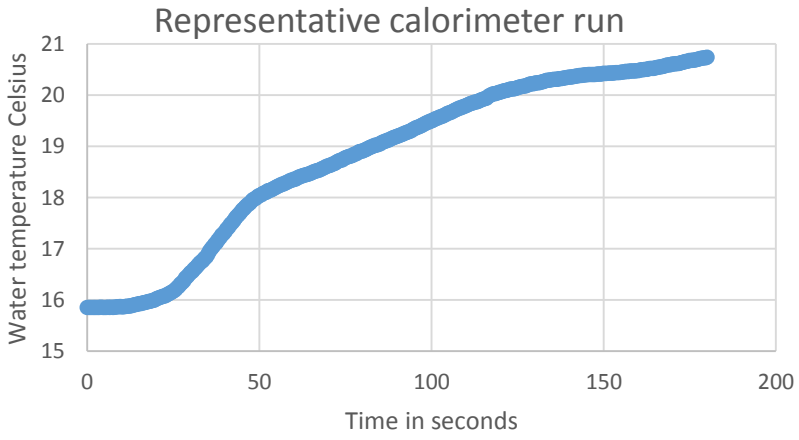

Table 2: Calorimetry data for CRC obtained from the hydrothermal carbonization of apples.

Initial water temperature (^oC)	Maximum water temperature (^oC)	Heat of combustion for burn mixture(J/g)	Corrected heat of combustion for CRC (KJ/g)
15.9	21.0	2133.84	11.65
15.9	21.2	2217.52	12.11
16.0	21.5	2301.20	12.56

Weight of CRC/KNO_3burn mixture: 0.5 g, weight fraction of CRC in burn mixture: 0.625, weight of water: 50 g, the heat of combustion for the burn mixture was multiplied by 5.46 to obtain the corrected heat of combustion for the CRC.

Table 3: Heat of combustion values for some components of biomass.

Source of CRC	starch	oranges	carrots	apples
Heat of combustion (KJ/g) ± %RSD	7.29 ± 2.4	12.73 ± 1.1	13.53 ± 2.1	12.11 ± 3.8

The heat of combustion of CRC produced from oranges, carrots and apples (5) was similar to that of lignite coal (6) indicating that the calorific value of biomass can be increased considerably by hydrothermal carbonization. The heat of combustion of starch was approximately half that of lignite coal, probably due to the fact that it consisted of only one type of molecule which did not produce as much carbon-enrichment upon HTC as the other components of biomass did.

Conclusions

It was possible to measure the heat of combustion of carbon-rich-compounds obtained by hydrothermal carbonization using a home-made calorimeter. It was necessary to use an oxidizer such as KNO_3 to enable uniform, complete and reproducible burning of the CRC. The heat lost by the calorimeter to the surroundings was calculated by measuring the heat of combustion of magnesium metal whose value was available from the literature. The correction factor accounted for both the weight fraction of the CRC in the burn mixture and the heat lost to the surroundings. Using the calorimeter constant, the heat of combustion of various components of biomass were calculated and found to agree reasonably well with previously reported values.

Further studies will investigate the effect of HTC process conditions, such as pressure, temperature and concentration on the magnitude of the calorific value of CRC obtained.

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