A User-Friendly Set up for Undergraduate Research: Combining Thermogravimetric Analysis with Micro Gas Chromatography

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Introduction

Investigated coupling TGA/DSC (Thermal Gravimetric Analyzer with Differential Scanning Calorimetry) with a portable Micro-GC (Gas Chromatography) to:

- perform common catalyst characterization tests (instead of a chemisorption unit)
- act as an easy reactor system for gas/solid reactions

In small research labs, this system allows for more versatility (since a TGA and Micro-GC can be used for multiple purposes).

Instrumentation

Thermal Gravimetric Analyzer (TA Q600)

- Offers the possibility of simultaneous measurement of weight change and true differential heat flow (differential scanning calorimetry (DSC)
- Can test to 1,500˚C

Figure 1: Thermogravimetric Analysis / Differential Scanning Calorimetry

INFICON Micro GC Fusion Gas Analyzer

- Portable gas chromatography with extremely short analysis time
- Provides ppm to % level detection
- User friendly front panel display and embedded browser-based software
- Configured with a 10 m Molecular Sieve 5A (Argon) and 8 m Q-Bond Plot columns (Helium)

Figure 2: Micro Gas Chromatography

Experimental Design

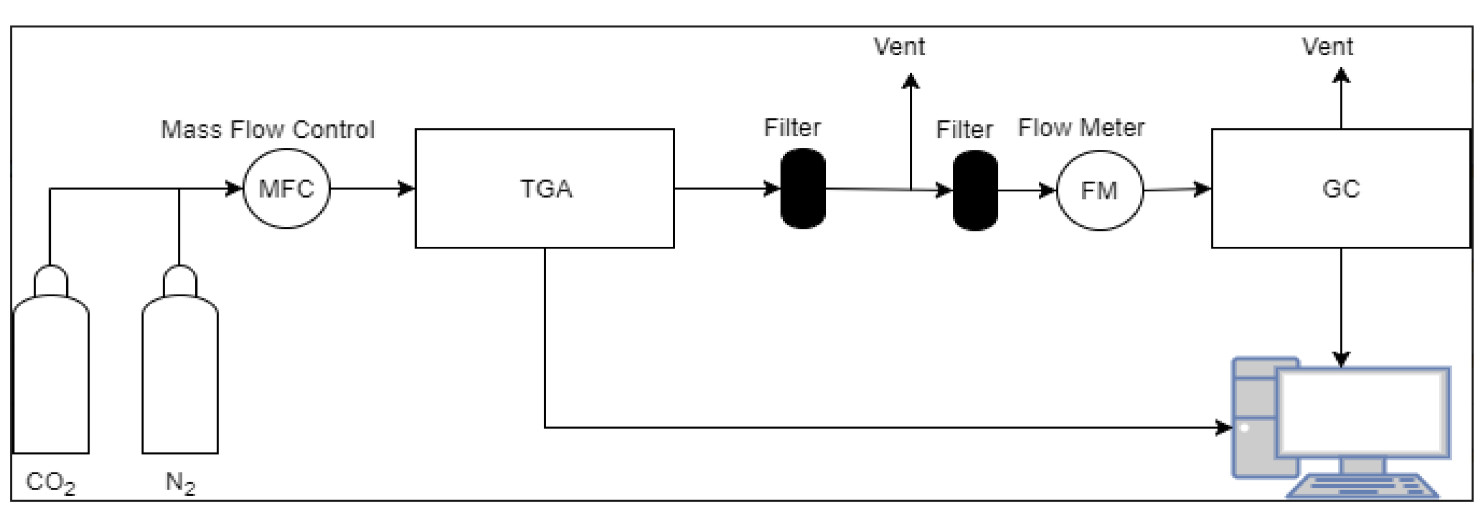


Figure 3: Schematic of the set up: TGA connected to the Micro GC

This set up was used to test the following solid/gas reactions:

- TPR on 10% Cu/Al_2O_3
- TPO on biochars (C_xH_y)
- Dry Gasification (CO_2) of biochars

Biochars were produced from Acorns or Oakheart by pyrolysis in Argon at 500C.

Figure 4: TGA/DSC connected to the Micro GC gas analyzer

TPR Data

Temperature Programmed Reduction (TPR) shows reduction behavior of an oxidized catalytic metal providing important information about the active metal.

Oxidized Catalytic Material + H_2 → H_2O + <H_2 + Reduced Catalytic Material

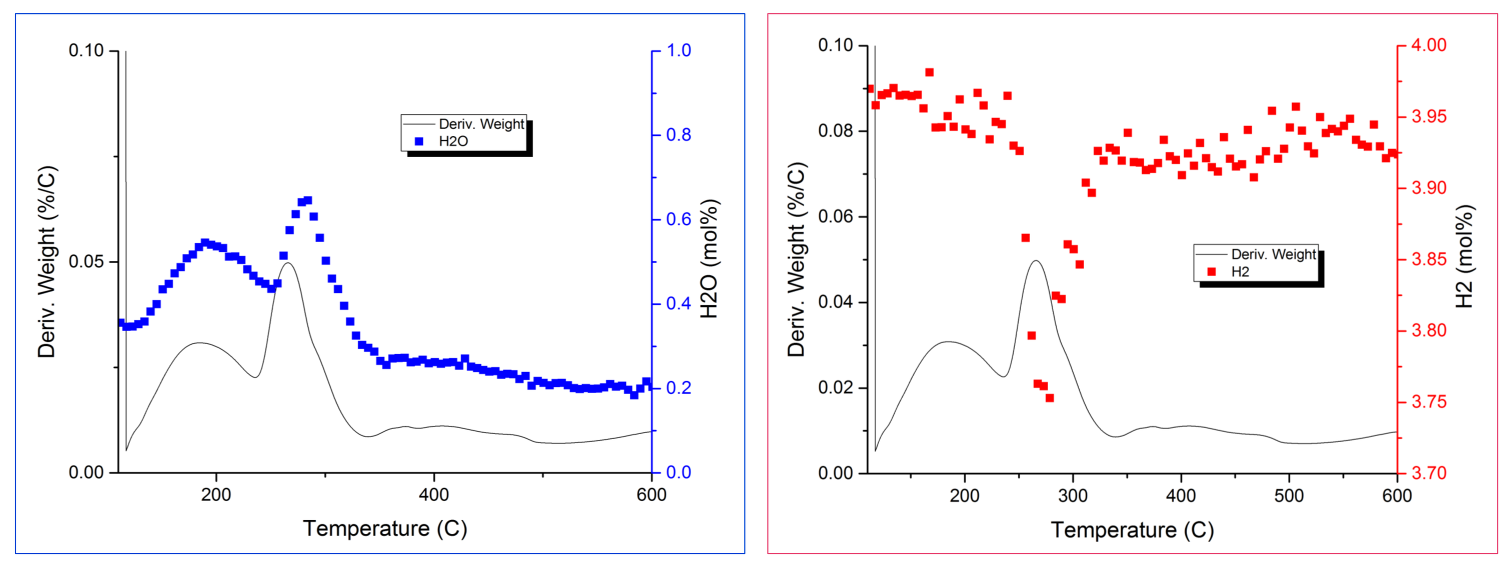


Figure 5: Water produced and hydrogen consumed during Temperature Programmed Reduction tests on a 40 mg 10% Copper catalyst with 4% H2/N2 at 100 mL/min total flow.

TPR data demonstrates:

- Micro-GC data confirmed what was measured on the TGA, and was in close agreement
- Micro GC measured both hydrogen depletion and water production, and could be optimized for either signal (water signal optimized in Figure 5).

TPO Data

Temperature Programmed Oxidation (TPO) tests are commonly used to measure the amount or type of carbonaceous species on a catalytic surface:

Catalytic material with carbon + O_2 → CO_2 + CO + <O_2 + carbon-free material

TPO tests can also measure oxidation of a metal, combustion behavior of a hydrocarbon sample, or to measure relative C/H ratios of a biomass sample.

$$C_xH_y + O_2 \rightarrow xCO_2 + yH_2O$$

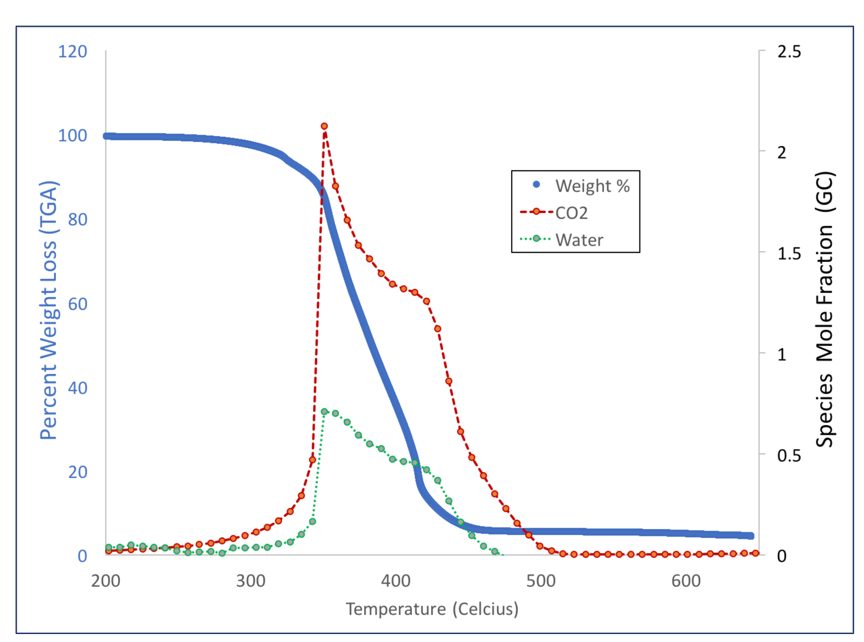


Figure 6: Gases produced (measured by micro-GC) and %weight loss (measured by TGA) during a Temperature Programmed Oxidation of a 30 mg biochar sample (ground acorn nutmeat). Ramp rate = 5°C/min with 100% air at 100 mL/min total flow.

CO_2 and H_2O concentrations could be integrated to determine the C/H ratio of biochar samples, which could not be done with a typical chemisorption unit.

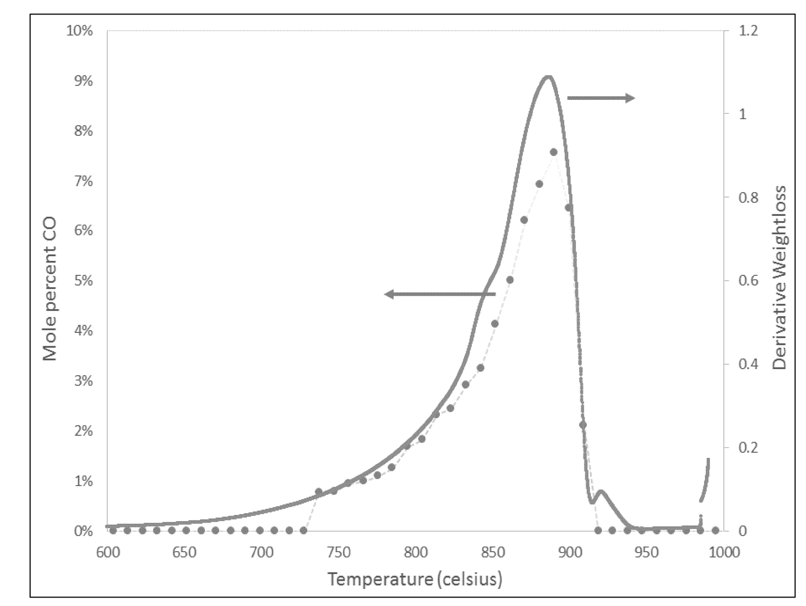
Biochar Sample	C:H Mol Ratio
Oakheart	3.4
Acornhat	3.7
Acornshell	2.4
Nutmeat	4.0
Acornshell	2.2

Figure 7: C/H ratio of several biochar species calculated from TPO

Gasification Data

Temperature programmed Dry Gasification, using CO_2 (the reverse Boudouard reaction) was investigated on various biochars.

$$CO_2 + C \rightarrow 2CO$$



Gas analysis was able to confirm that we were measuring weight loss due to dry gasification on the TGA.

Figure 8: Derivative weight loss (measured by TGA) and concentration of carbon monoxide (measured by micro-GC) with ramp rate of 5°C/min in 100 mL/min 5% CO_2/N_2.

Benefits for biomass research A TGA without gas analysis could analyze only the temperature that pyrolysis occurs, or the ash content. However, we were able to quantify gas species (including H_2 - difficult to measure with mass spectrometry). Thus we were able to measure C/H ratios of our samples and confirm gasification products above.

Conclusions + Recommendations

Some primary benefits of the set-up:

- Versatility: both instruments were used on other projects in the lab, and the INFICON Micro-GC was easily portable allowing for the two instruments to easily have multiple uses.
- Ease of use: undergraduate researchers were able to quickly learn and grasp both techniques, and easily analyze data from both instruments. Both instruments were robust enough for independent use. Embedded Micro-GC software allowed for quick learning for students.
- Sample rates: the Micro-GC was able to complete runs quickly (on order of 1 sample per minute) so samples could be synced between instruments.

In the future we would:

- Use a heated transfer line and reduce residence time in transfer line.
- Maximize TGA sample cup sizes to increase signal size.

Acknowledgements

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