TA Instruments – Application Note

Microcalorimetry: A Useful Tool for Biofuel Testing

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Introduction

One of the key initiatives from the U.S. Department of Energy in recent years is to set goals to replace some portion of the fossil fuels used for energy generation with biofuels. This has led to a large increase in the funding dedicated to biomass based research. The conversion of renewable biomass to useable and sustainable fuels is already underway to address growing energy demands. To effectively generate the knowledge base to make a biomass conversion process an economically viable endeavor, the demands for the appropriate tools and tests for studying and characterizing biofuels are also increasing. This application note presents several examples of how microcalorimetry based assays can be used for the characterization of biofuels. These examples show how to address several biofuel related concerns utilizing the features and performance characteristics of the multi-cell differential scanning calorimeter (MC DSC).

Experimental

The MC DSC instrument was equilibrated at 25˚C prior to all of the studies. An external cooling bath was set to 20˚C and when operating below the dew point a steady flow of N_2(g) was supplied at 20-30 mL min^{-1} to ensure that the electronic housings remained dry. The MC DSC can be equipped with four different types of ampoules, including a high pressure, batch, and probe accessible, along with the standard closed ampoule. For the examples presented in this paper, all samples were placed into closed Hastelloy ampoules with hermetic seals for pressures up to 15 atmospheres. The samples for both waxing and lignin content were assayed by temperature scanning and the kinetic assay (transesterification) was performed isothermally.

Results and Discussion

Waxing

One problem with biologically derived fuels is the potential for waxing that occurs at low temperatures, rendering them useless. Characterization of the “cloud point” and the lower temperature “pour point” are important when considering storage, transportation and use. In a differential scanning calorimeter (DSC) the waxing is observed as a first order phase transition and is typically reported as a wax appearance temperature (WAT).

The WAT is closely related to the "pour point" of the fuel which is traditionally measured by viscometry (1). Other groups have extended the analysis of biofuels on a DSC and use the thermogram data to quantitate the wax content. In most cases, the wax content determined by DSC substantially agrees with that determined with the industry accepted standard acetone method (2). Each sample was shaken prior to loading ~ 500 mg into individual ampoules. The data in figure 1 shows one cooling scan. The WAT was observed at 10.0 ˚C for the animal derived fuel and was absent in the soy derived fuel. Fitting a sigmoid baseline to the animal derived biofuel data yields a Q of 18.0 J/g. Repeating the cool scan on the same sample gave data that resulted in a Q value that agreed with the first value within less than 0.5%. This indicates that this process is reversible in the range of 0 to 70 ˚C. Using equation 1 found in the Chen paper (%wax content = 0.75 x Q +0.20)(2), the wax percentage of this sample was determined to be 13.7 %.

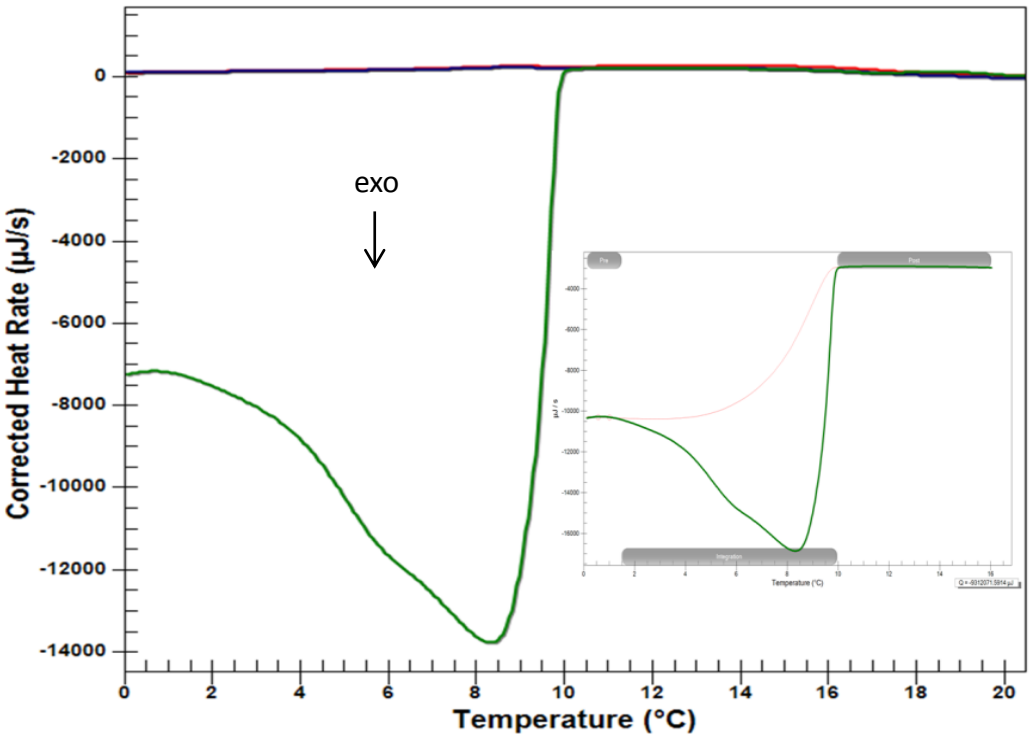

Figure 1. (A) The blue and red lines are for soy derived biodiesel and the green scans are the animal derived biodiesel. The inset shows the baseline applied for area integration of Q.

Lignin Content

The efficiency of some biomass conversions depends on hydrolyzing agents gaining access to plant polysaccharides (3). One of the largest factors affecting efficient energy sequestration is the

biodegradation of lignin. Degradation of this polymer is a prerequisite for processing biofuels and improving lignin degradation would optimize the output from biofuel processing (3). The presence of lignin in a piece of wood sample was observed via DSC (Figure 2). The larger ampoules of the MC DSC enable the detection of this material; the larger sample size enables detection of weak or low signals. Prior to placing the sample of wood into the MCDSC ampoule, it was pressure and temperature treated in a vacuum oven to remove water that would have saturated the heat flow signal.

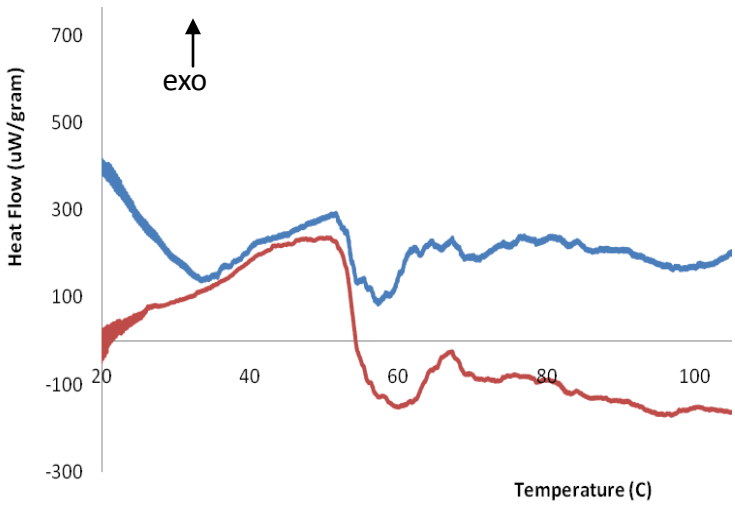

Figure 2. (A) Overlay of normalized and background resolved data collected on a MC-DSC. The glass transition is attributed to the lignin content in the woody sample.

Biofuel Development

Transesterification is a key step to produce safe fuels from vegetable oils (4). Determination of the rate, as well as further optimization of this turnover, can be investigated with different formulations. In the example shown in Figure 3 a 25˚C isothermal experiment was performed in a MC DSC. The transesterification of the soybean oil and alcohol to the ethyl ester was catalyzed by a caustic agent in this case, 3% w/v sodium hydroxide. Turnover can be optimized or investigated with different oils, alcohols, and catalyst agents.

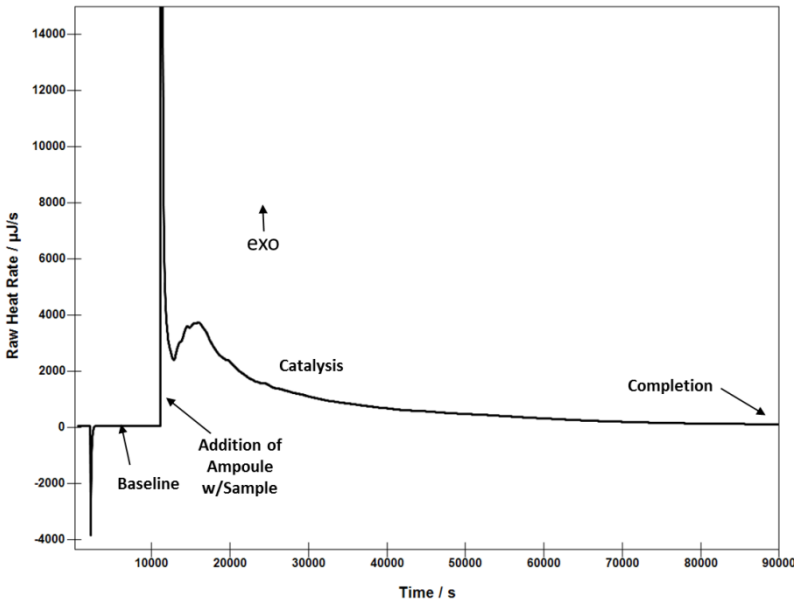

Figure 3 Biofuel production via transesterification of soy bean oil.

Conclusions

The MC DSC, has the features and performance characteristics for reliable and effective characterization and optimization of biofuels. In the scanning mode, the WAT and presence of lignin were both identified. In an isothermal mode, the catalytic process of fuel production was characterized. A large sample volume, 1.0 mL, and dynamic range, -40 to 150˚C, as well as the ability to run either isothermally or scanning (up to 2˚C/min) makes the MC DSC a flexible analytical tool for characterizing the molecular reactions required for producing biofuels and for understanding the quality of the final product.

References

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