Analytical Method Development for the Analysis of Biomass Degradation Products

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Abstract

The goal of this project is to study the kinetics of hydrothermal liquefaction of biomass. Biomass contains stored chemical energy that can be converted to renewable liquid and gaseous fuels through various processes, but an in-depth understanding of the kinetics of these processes is important in order for them to be feasible on a large scale. Since biomass degradation products depend on the type of biomass used as well as the reaction conditions, this task can be quite complicated. To minimize complications in our initial studies, we will use D-glucose as the starting material. To better understand the degradation pathway's dependence on reaction conditions, qualitative and quantitative analysis will be done on the products of hydrothermal degradation of D-glucose after various reaction times and conditions. However, the appropriate analytical techniques must be identified and tested first to ensure they are capable of identifying and quantifying biomass degradation products. The analytical techniques tested for this analysis include nuclear magnetic resonance (NMR), gas chromatography-mass spectrometry (GCMS), and high-performance liquid chromatography (HPLC).

Introduction

Because of the many issues surrounding the usage of fossil fuels – whether it be the fluctuating supply, the associated cost, or environmental effects – there is gravitation towards sustainable sources of energy. A form of such sustainable energy can be found as biomass which is classified as renewable organic material derived from plants and animals. Harnessing this energy entails understanding the kinetics behind biomass degradation products. To quantify and qualitatively identify products of D-glucose's degradation, it is necessary to have the appropriate instrumentation that can provide reliable results. Each analytical technique requires the optimization of several parameters and sufficient knowledge of the theory behind the method. While this process is time consuming, it is essential to establish which instruments will be most useful for subsequent steps in this research.

NMR

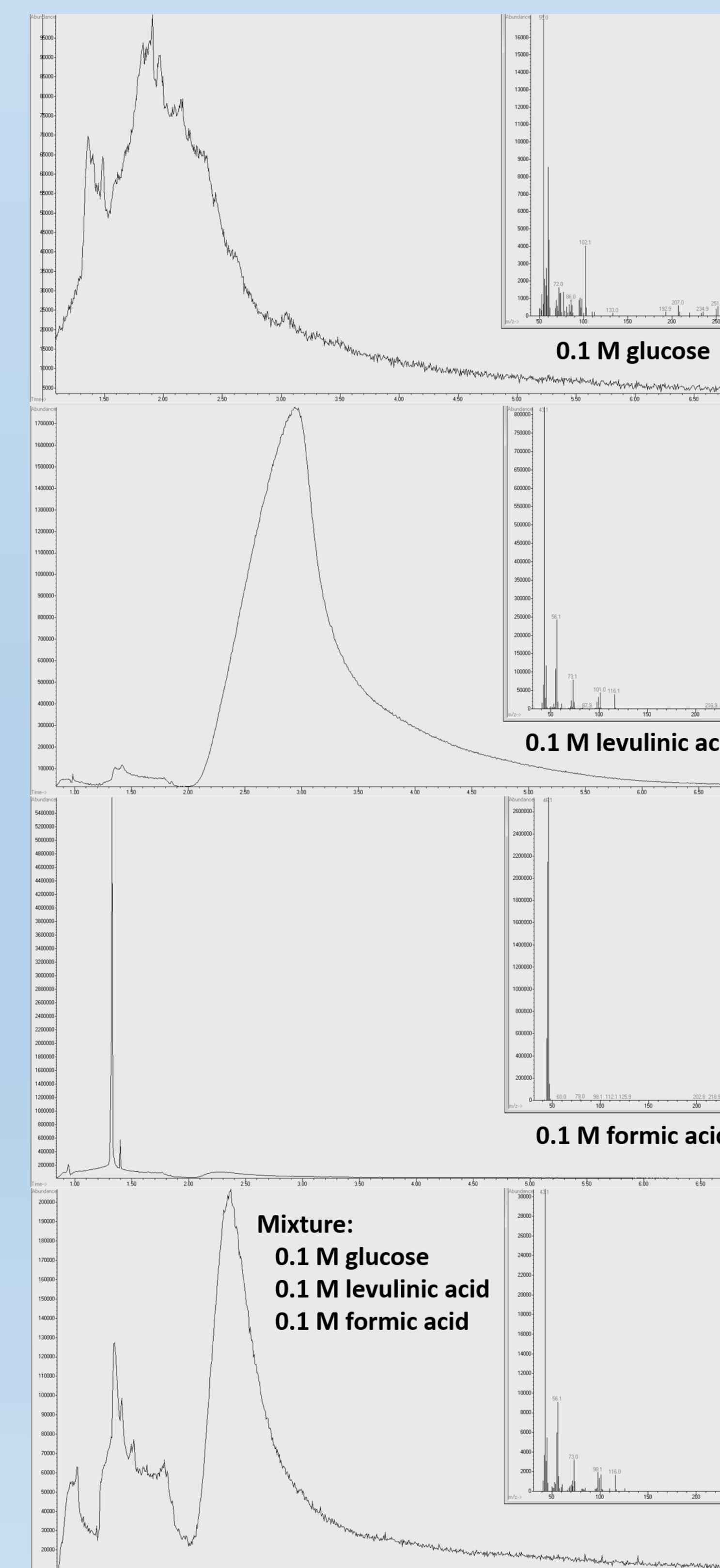
NMR spectroscopy works on the basic principle of emitting low energy radio waves that interact with the nuclear spin of molecules. The applied magnetic field allows for the measurement of energy difference between spin states to achieve resonance of protons in the compound. While nuclear magnetic resonance is often used in research that involves structural analysis, it may also be used for identification of components in a mixture. The use of NMR in our research is desired to be used in addition to HPLC to confirm the identity of the substances we are analyzing.

Our data was collected on Anasazi Eft-90 NMR Spectrometer. Since our samples are in aqueous solution, a water-suppression sequence was used to minimize the solvent signal and thus increase the resolution of the solute signals. The pre-programmed water-suppression sequence available did not adequately suppress the water signal, thus a better water-suppression sequence must be programmed before useful NMR spectra can be obtained. However, this instrument is designed for the classroom setting rather than research, so setting up more complex experiments is more difficult than on research instruments and may not be possible.

GCMS

In gas chromatography, a volatile liquid analyte is injected, vaporized, moved through the column by a carrier gas, and interacts with the stationary phase to elute compounds. Once the components are eluted from the column, they are ionized and detected by a mass spectrometer, yielding peaks that correspond to each components mass-to-charge ratio. To optimize data collection several parameters must be adjusted, this includes but is not limited to the injector and column temperatures as well as the flow rate of the carrier gas.

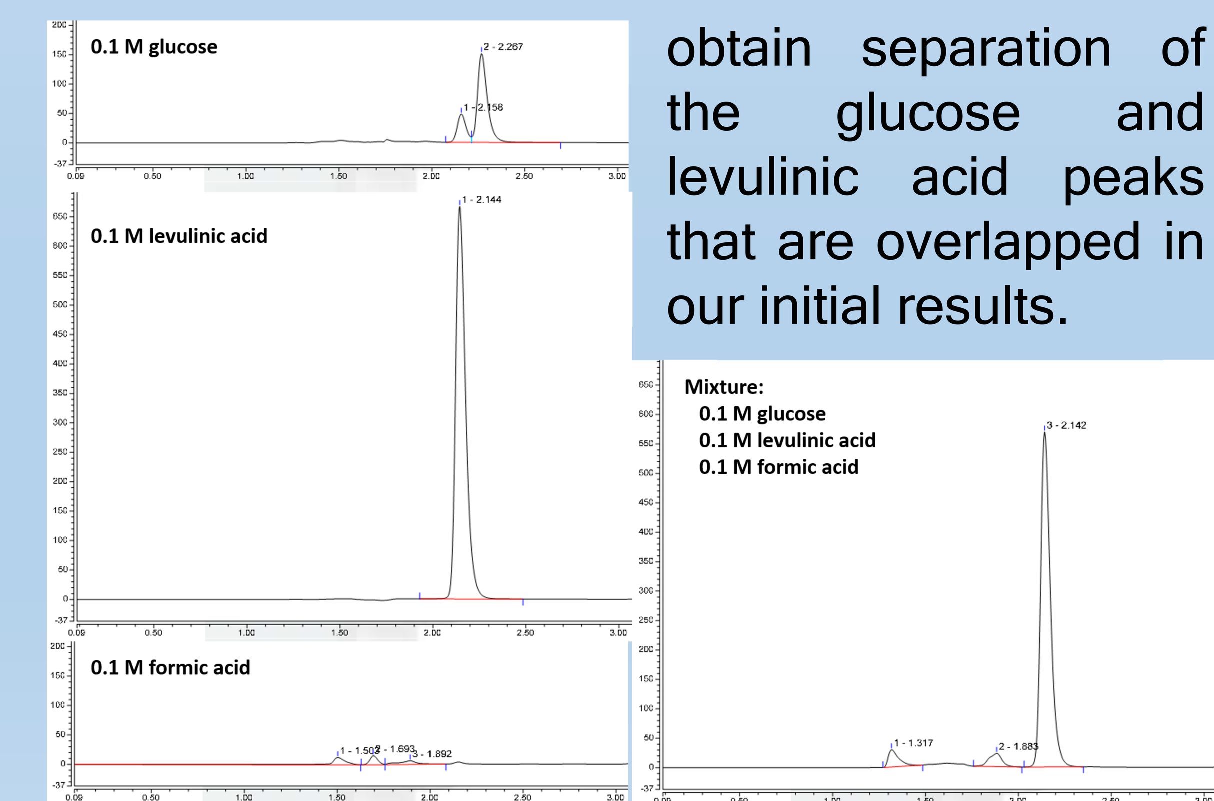
Our data was collected on Agilent 6890N GC paired with a 5973N MS. The instrument is equipped with a C_{18} column and uses helium as the carrier gas. The initial column temperature was set to 100°C and then ramped at various rates and to 250°C. This was found to help narrow some of the peaks, but did not improve the separation of the peaks. The sample concentrations tested were chosen to be similar to samples we will have in later steps of our research. Since the glucose and levulinic acid peaks were very broad we also tested diluted samples, but it only resulted in more noise instead of sharper peaks. Increasing the flow rate of the carrier gas also did not help to reduce the peak widths, so the default of 3ml/min was used for all samples. For now, the use of the GCMS for this project is not feasible as it presents a complex system of parameters that we currently do not have thorough understanding of.



HPLC

High-performance liquid chromatography utilizes high pressure to yield high-resolution separations for compounds. Solvent is forced through a packed column and interacts with a stationary phase made of fine particles. Flow rate and solvent choice are two notable parameters that must be optimized for each sample.

Our data was collected on a Dionex Ultimate 3000 HPLC. The solvent mixture used consisted of 40% methanol, 59% water, and 1% acetic acid at a flow rate of 1 ml/min. These parameters were used because it is a teaching instrument that was setup for a specific lab. For future analysis we will test water as the carrier solvent and reduce the flow rate to see if we can obtain separation of the glucose and levulinic acid peaks that are overlapped in our initial results.



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