Using Iron Enriched Biomass for fast pyrolysis to analyze the possible effects on vapor yield

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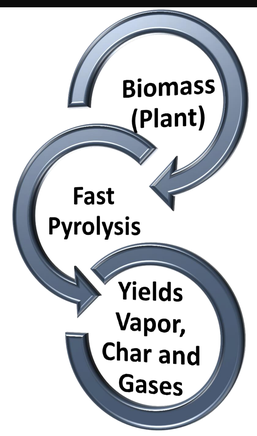
INTRODUCTION
Background and Importance overview

What is Fast Pyrolysis?

- Catalytic Fast Pyrolysis is a process in which a feedstock (biomass) is heated to temperatures of roughly 500°C, in the absence of oxygen, and the resulting vapors are subjected to oxygen removal using a catalyst. The purpose of this research is to improve the yield of fuel range products from biomass pyrolysis, and to eventually offset petroleum-based fuels, products, and energy with bio-based ones.



What issues are researchers facing in the biofuel Arena?

- The main issue that we are facing in regards to biomass fuel is the final yield of fuel range vapors produced from pyrolysis.

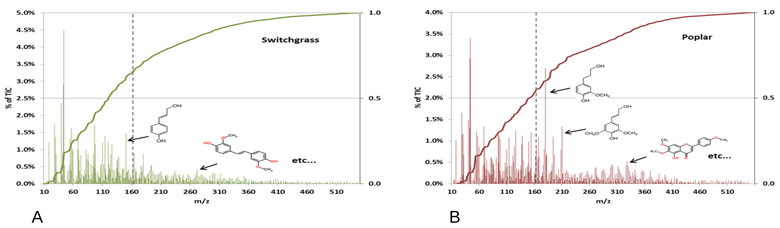


Figure 1: Mass Spectra of (A) Switchgrass and (B) Poplar pyrolysis products showing the wide variety of high molecular weight products that are difficult to upgrade. Much of the biomass carbon is contained in oxygenated molecules that are unstable and cannot be used for fuel.

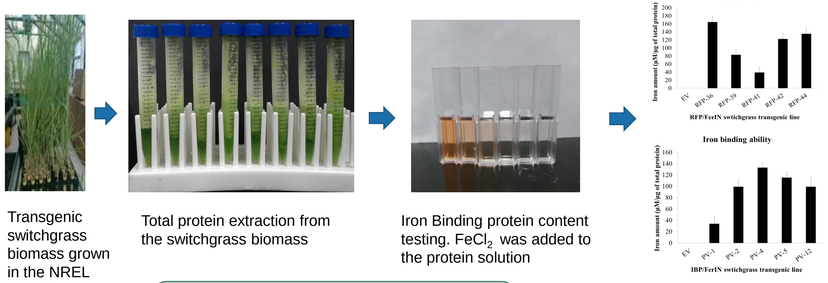
Experimental Approach

Use iron enriched biomass for pyrolysis. Iron has shown some potential to catalyze favorable reactions to produce higher liquid yields during pyrolysis, and is thought to target multiple bonds in plant cell wall polymer networks[1]. Our hypothesis is that if plants' uptake of iron during growth is increased, the iron can be a helpful catalyst during pyrolysis.

METHODS AND PROCEDURE
Biomass preparation and Pyrolysis

Iron Binding Protein Content Analysis

- The biomass' iron content was calculated by calculating the absorbance levels of the extracted iron binding protein



Transgenic switchgrass biomass grown in the NREL greenhouse

Total protein extraction from the switchgrass biomass

Iron Binding protein content testing. $FeCl_2$ was added to the protein solution

The iron content/ iron binding ability was then calculated from the absorbance graph from a spectrophotometer.

Based off the results from the Iron content bar graph, the samples with high Iron were chosen for ICP and for fast pyrolysis.

The selected biomass was then prepared by separating stem from leaf for each of the Poplar and Switchgrass then grinded into 20 mesh and weighed in boats of 20mg

Molecular Beam Mass Spectrometer (MBMS)

For this experiment we coupled a pyrolysis reactor to a MBMS. The biomass would be placed into the reactor set to 500°C. Argon was used as a tracer gas, while Helium was an inert carrier. The the vapors from pyrolysis would then flow through an orifice and into the MBMS and through an electron beam where the concentrations of the different molar masses will be measured and displayed on a mass spectra.

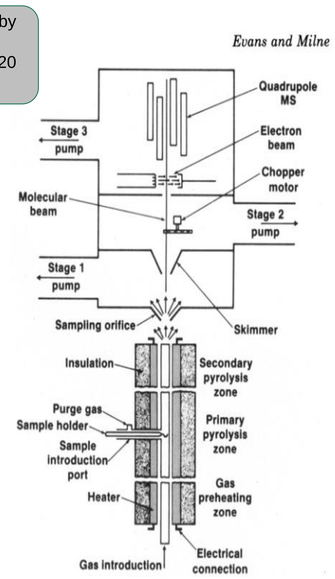
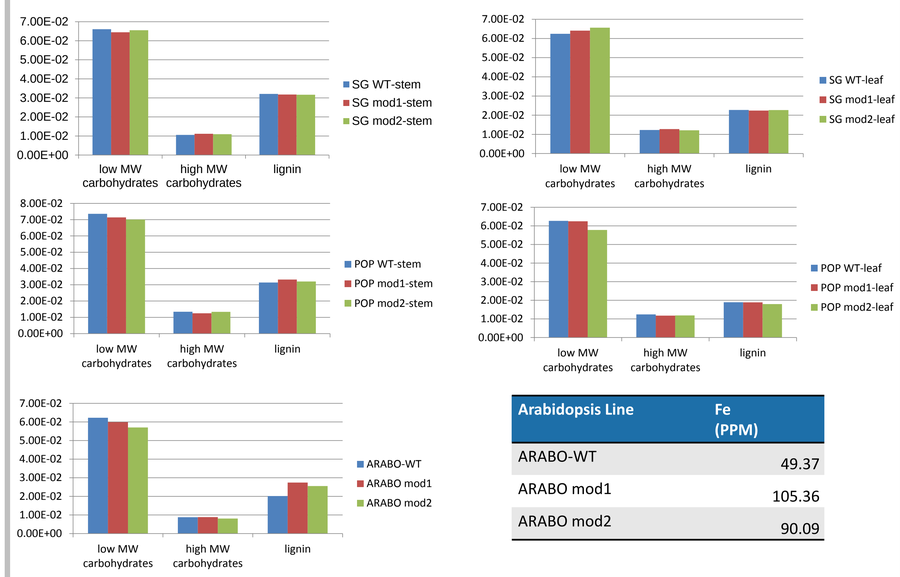


Figure 2: Schematic of pyrolysis vapor generator coupled to a molecular–beam mass spectrometer sampling system.

MBMS SPECTRA AND DATA ANALYSIS
Results and Discussion

Mass Spectral Average and Normalization

- The following graphs show the important groups of peaks observed with the MBMS for the transgenic biomass.



Arabidopsis Line	Fe (PPM)
ARABO-WT	49.37
ARABO mod1	105.36
ARABO mod2	90.09

- The normalized mass spectra displays minor changes in the lignin content of the transgenic Poplar and Switchgrass biomass. While the Arabidopsis shows overexpressed lignin content once pyrolyzed. There is a visible trend in the low carbohydrates of the Arabidopsis and Poplar leaves and stem.

FUTURE RESEARCH
How has the Iron effected the way Biomass growing and harvesting is done

How does enhanced iron binding affect biomass growth, and how do changes in pyrolysis vapors impact catalytic fast pyrolysis yields?

- The next step in addressing the effects of iron accumulation in plants is using a zeolite, ZSM5 catalysis with fast pyrolysis. ZSM5 has the ability to upgrade and convert pyrolysis vapors into hydrocarbons which will provide a greater understanding on aromatics formation and how biomass can be improved for thermochemical conversion[2].

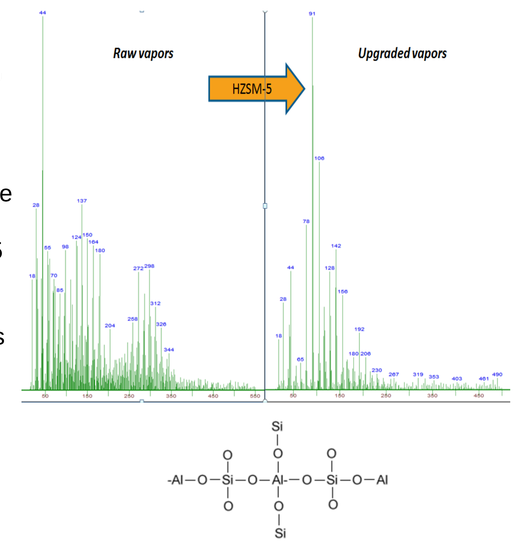
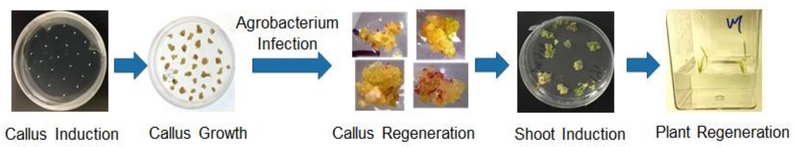


Figure 3:Zeolite Catalyst ZSM5

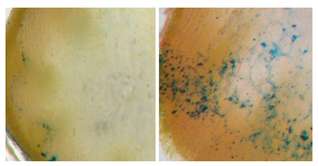
METHODS AND PROCEDURE
Biomass preparation and Pyrolysis

Transgenic Biomass Preparation

The feedstock used for this experiment was infected by *Agrobacterium*. This unicellular species releases DNA plasmid into cells of the host plant which then becomes part of the genome of the plant. This plasmid was genetically modified to translate into an increase of iron binding protein that the plant would produce. Thus, the protein binding content would increase the plants iron uptake during growth.



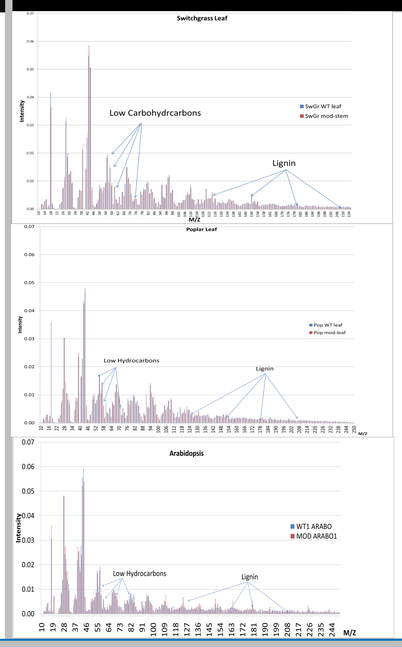
Figures: courtesy of Chien-Yuan Lin



This image displays the use of Prussion Blue staining to track the Iron storage in plants. With this it was found the plants such as Hybrid Poplar stores more iron in leaves than stem.

Figure courtesy of Bryon Donohoe

MBMS SPECTRA AND DATA ANALYSIS
Results and Discussion



Mass Spectra Results

- The mass spec for the biomass was collected for each samples stem and leaf separately. The leafs of each of Poplar and Switchgrass are thought to accumulate more iron than the stem. As displayed in the graphs, the results show that they both have little to no difference from the wild type line of the plant. The red and blue lines are inseparable. While there is a large change in the lignin expression of the Arabidopsis.

Arabidopsis has been found to accumulate iron in consistent proportions throughout tissue and was the first plant at NREL to be modified with ferritin, Iron binding protein.

ACKNOWLEDGMENTS
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References:

1- Wei, Hui et al. "Transgenic Ferritin Overproduction Enhances Thermochemical Pretreatments In Arabidopsis." Biomass And Bioenergy, vol 72, 2015, pp. 55-64. Elsevier BV, doi:10.1016/j.biombioe.2014.11.022
2-Ramirez-Corredores, M.m. "Pathways and Mechanisms of Fast Pyrolysis." The Role of Catalysis for the Sustainable Production of Bio-Fuels and Bio-Chemicals, 2013, pp. 161–216., doi:10.1016/b978-0-444-56330-9.00006-1.

Figures:

Decorative Pictures courtesy of: Michigan Tech, echofriend.com, agbiochem, CBD oil, globe-net.com
Figure 1:Carpenter, D., Mukarakate, C., Budhi, S. and Lee, D. (2015). The Effect of Feedstock on Catalytic Upgrading of Biomass Pyrolysis Vapors
Figure 2: Evans, R. and Milne, T. (1987). Molecular characterization of the pyrolysis of biomass. Energy & Fuels, 1(2), pp.123-137.
Figure 3: Courtesy of Green Chemistry.

Conference Title
Conference Location: City, State
Conference Dates

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