INL/MIS-22-66293-Revision-0

Understanding Biomass and Polymer Feedstock Variability Through Analytical Pyrolysis and Two Dimensional Gas Chromatography and Mass Spectrometry

Changing the World's Energy Future

Brittany D Hodges, Christopher A Zarzana, Grace A. Castle

Idaho National Laboratory

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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Understanding Biomass and Polymer Feedstock Variability Via Analytical Pyrolysis and Two Dimensional Gas Chromatography Mass Spectrometry

Brittany Hodges
Research Scientist, Idaho National Laboratory

Grace Castle, Gary S. Groenewold, **Christopher Zarzana,**
Idaho National Laboratory, Idaho Falls, ID

March 4,2022

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INL/CON-20-58531

Overview:

- What is Biomass? Why do we care about variability and characterization?
- What are the tools we use in our lab to understand
- Project 1: Understanding effects of corn stover microbial self-heating
- Project 2: Macromolecule radiolysis with radical capping donors
- Conclusions

Project 1:

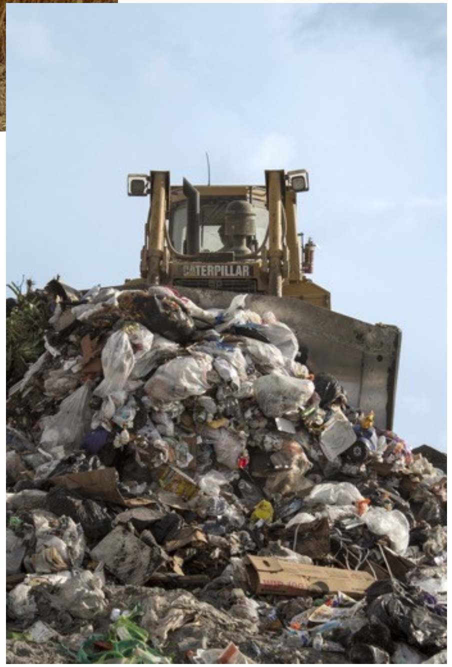
Signatures of Biologically Driven Hemicellulose Modification Quantified by Analytical Pyrolysis Coupled with Multidimensional Gas Chromatography Mass Spectrometry

What is Biomass?

Photosynthesis

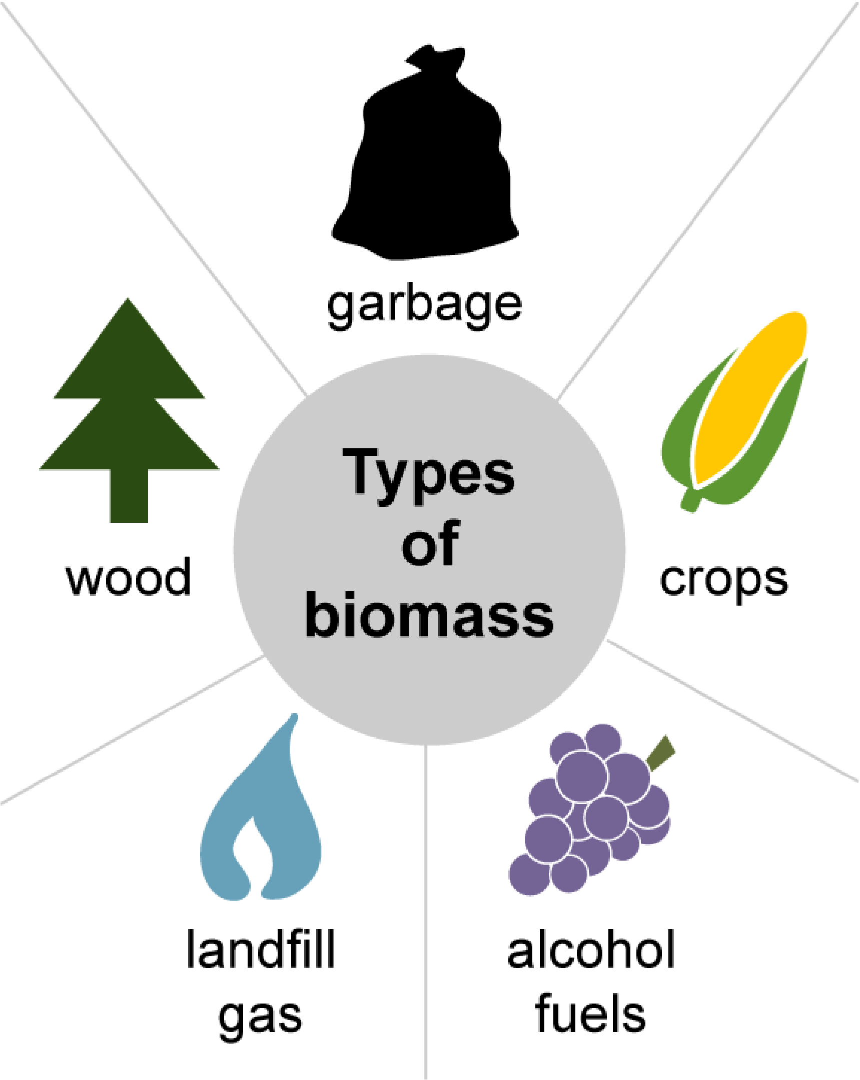
In the process of photosynthesis, plants convert radiant energy from the sun into chemical energy in the form of glucose—or sugar.

(water)		(carbon dioxide)		(sunlight)		(glucose)		(oxygen)
$6\,H_20$	+	$6\,CO_2$	+	radiant energy	$\rightarrow$	$C_6H_{12}O_6$	+	$6\,O_2$

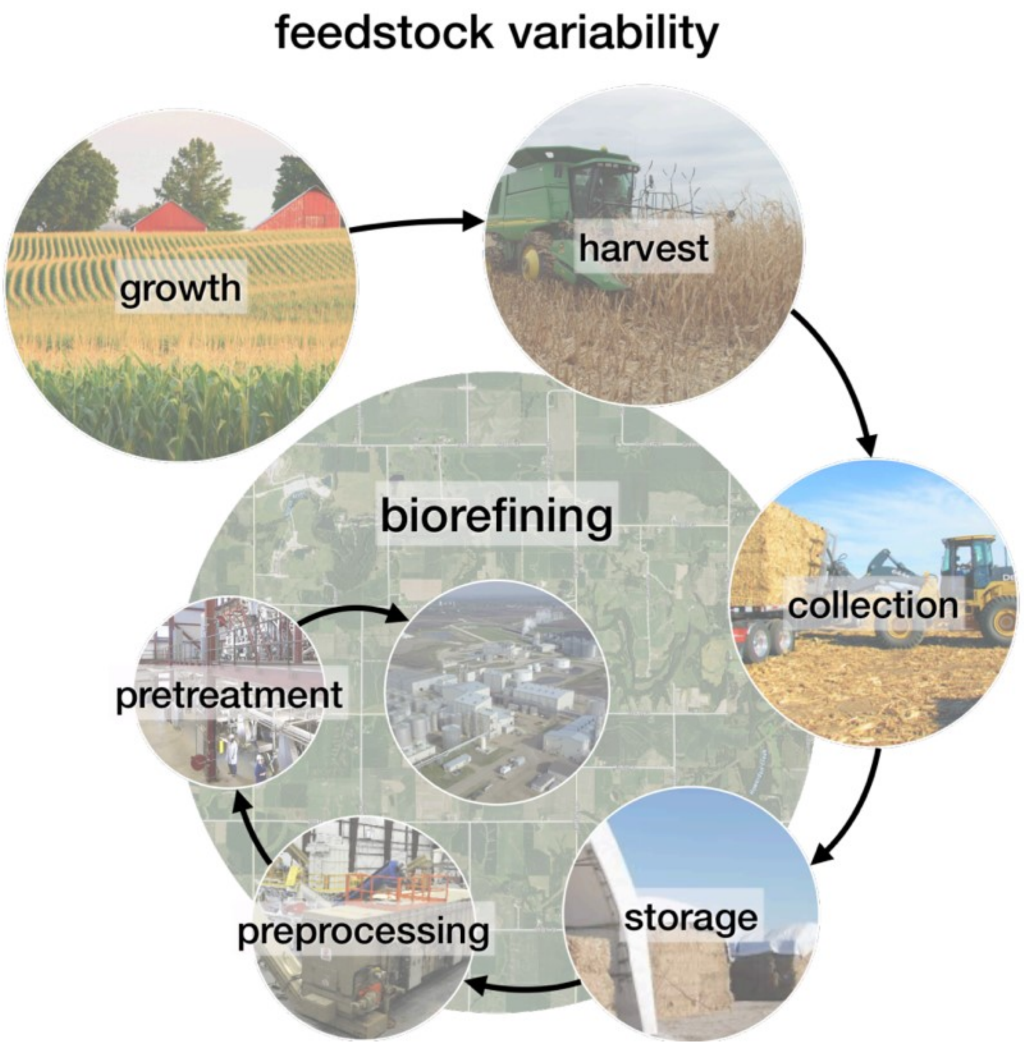


Adapted from The National Energy Education Project (public domain)

Types of Biomass

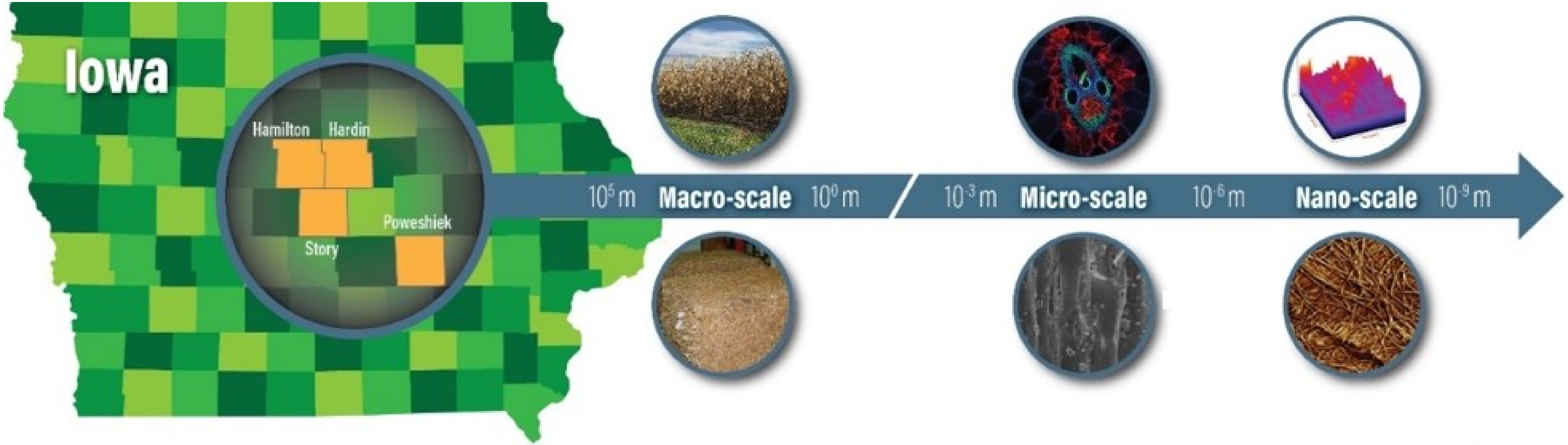


Biomass attributes can vary due to inputs at every step of the process, from growth to biorefining



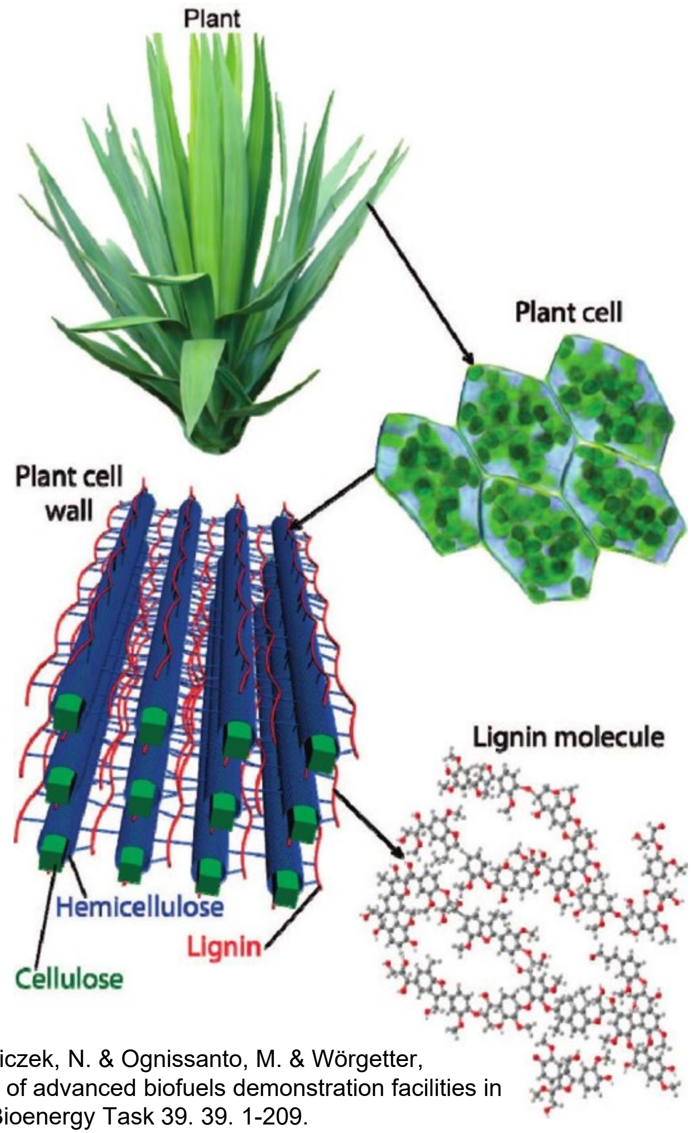
Ray, et al. 2020, *ACS Sus. Chem. Eng.* https://doi.org/10.1021/acssuschemeng.9b06763

Factors from the Macro-Scale to the Molecular Scale Influence Biomass Feedstock Variability



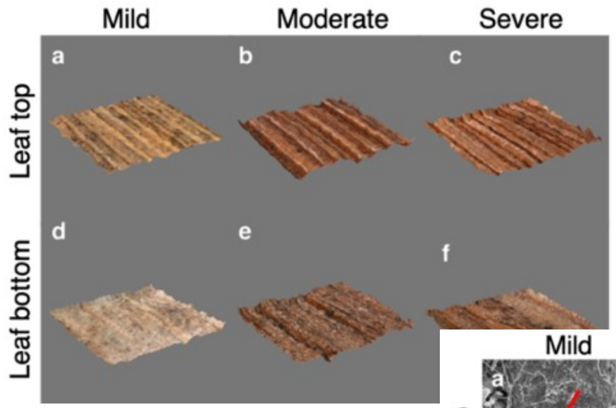
Macromolecules found in Biomass

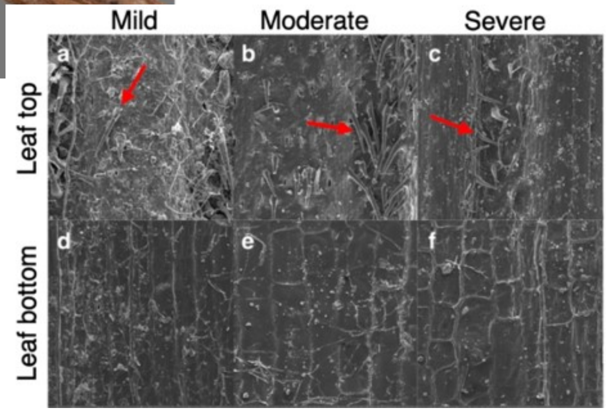
- **Cellulose**
  - organic polysaccharide in linear chain of several hundred to many thousands of β(1→4) linked D-glucose units.
  - Important structural component of the primary cell wall of green plants. $(C_6H_{10}O_5)_n$
  - Cellulose is crystalline, strong, and resistant to hydrolysis
- **Hemicellulose**
  - Matrix polysaccharides, present with cellulose in plant cell walls
  - Random, amorphous structure with little strength
  - Easily hydrolyzed
- **Lignin**
  - Complex organic polymers form key structural materials in the support tissues of vascular plants and some algae.
  - Important in formation of cell walls, especially in wood and bark
  - Lend rigidity and do not rot easily
  - Chemically, lignins are cross-linked phenolic polymers



Bacovsky, Dina & Ludwiczek, N. & Ognissanto, M. & Wörgetter, Manfred. (2013). Status of advanced biofuels demonstration facilities in 2012. A Report to IEA Bioenergy Task 39. 39. 1-209.

In-field storage of corn stover leads to microbial heating





Bose, Leal, et al., Submitted *ACS Sus. Chem. Eng.*

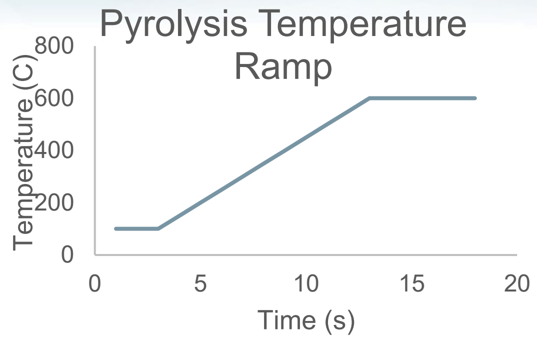
Overview: Molecular characterization approach to elucidate cell wall modifications in biologically degraded corn stover

- Analytical pyrolysis-GCxGC MS provides molecular-level information
  - Corn stover samples
    - microbial heating
    - Analyzed five bales with visual microbial degradation
      - Bales dissected into mild, moderate, and severe microbial heating conditions

- Analytical approach
  - Pyrolysis of samples
  - Analysis with gas chromatography and time of flight mass spectrometry
  - Quantitation with internal standard

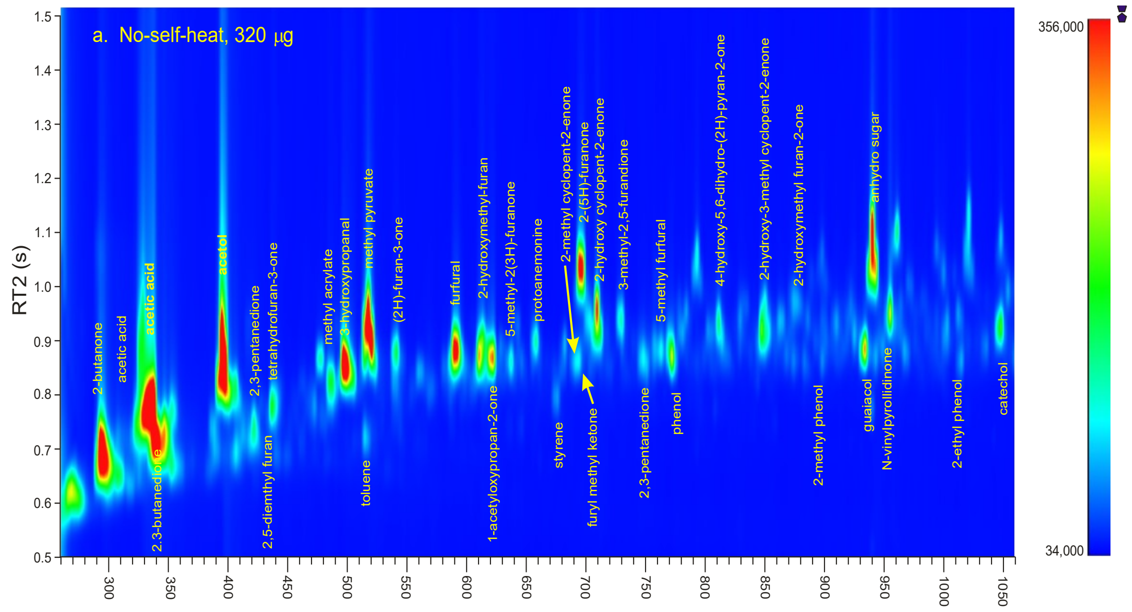
Methods

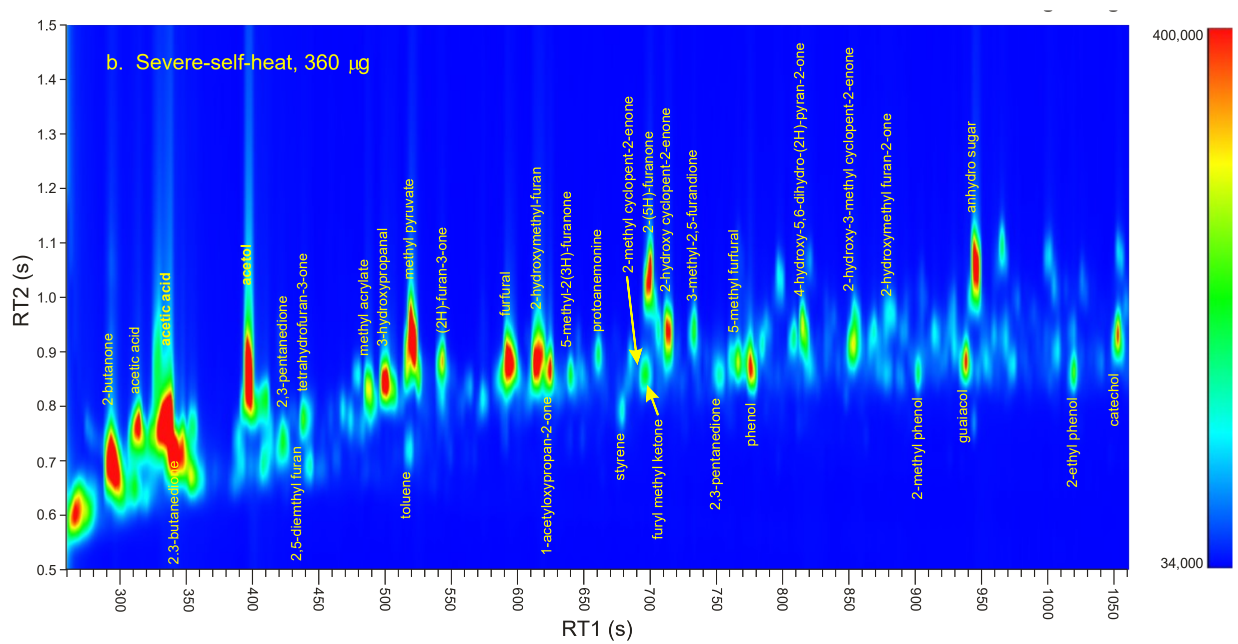
- Corn stover samples milled to >0.2 mm
  - 300 µg samples measured for pyrolysis
  - Internal Standard: 3 nanomoles 9-(9H)-fluorenone
- **Pyrolysis:** CDS Analytical 5250
  - Samples ramped from 100°C to T_{max} between 300-600 °C
- **Gas Chromatography:** Agilent 7890
  - Column 1: **Boiling Point Separation**
  - Column 2: **Compound Polarity Separation**
- **Mass Spectrometry:** Leco Pegasus 4D TOF



Leco GCxGC TOF MS with Pyrolyzer

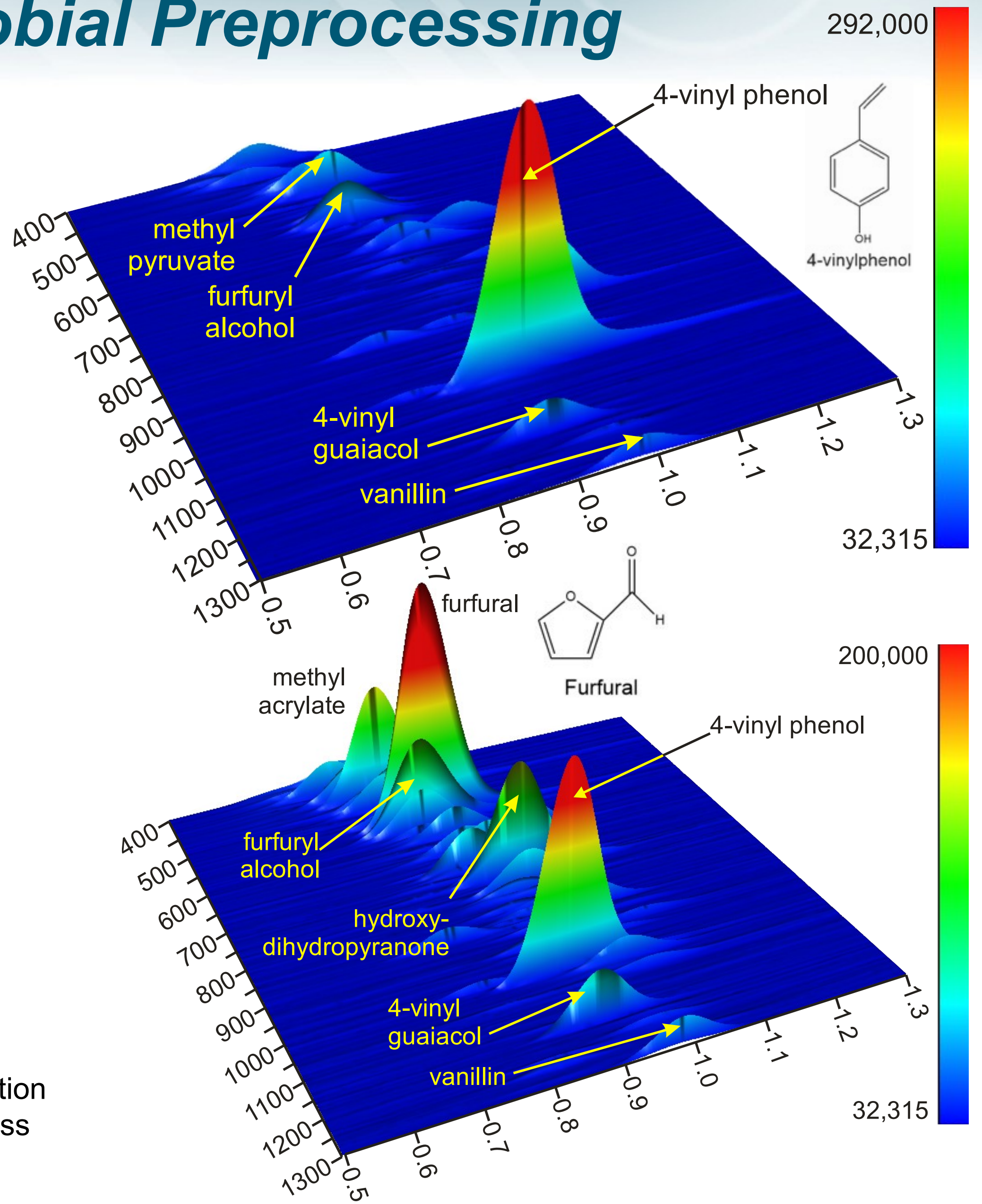
Chromatograms at 600 °C





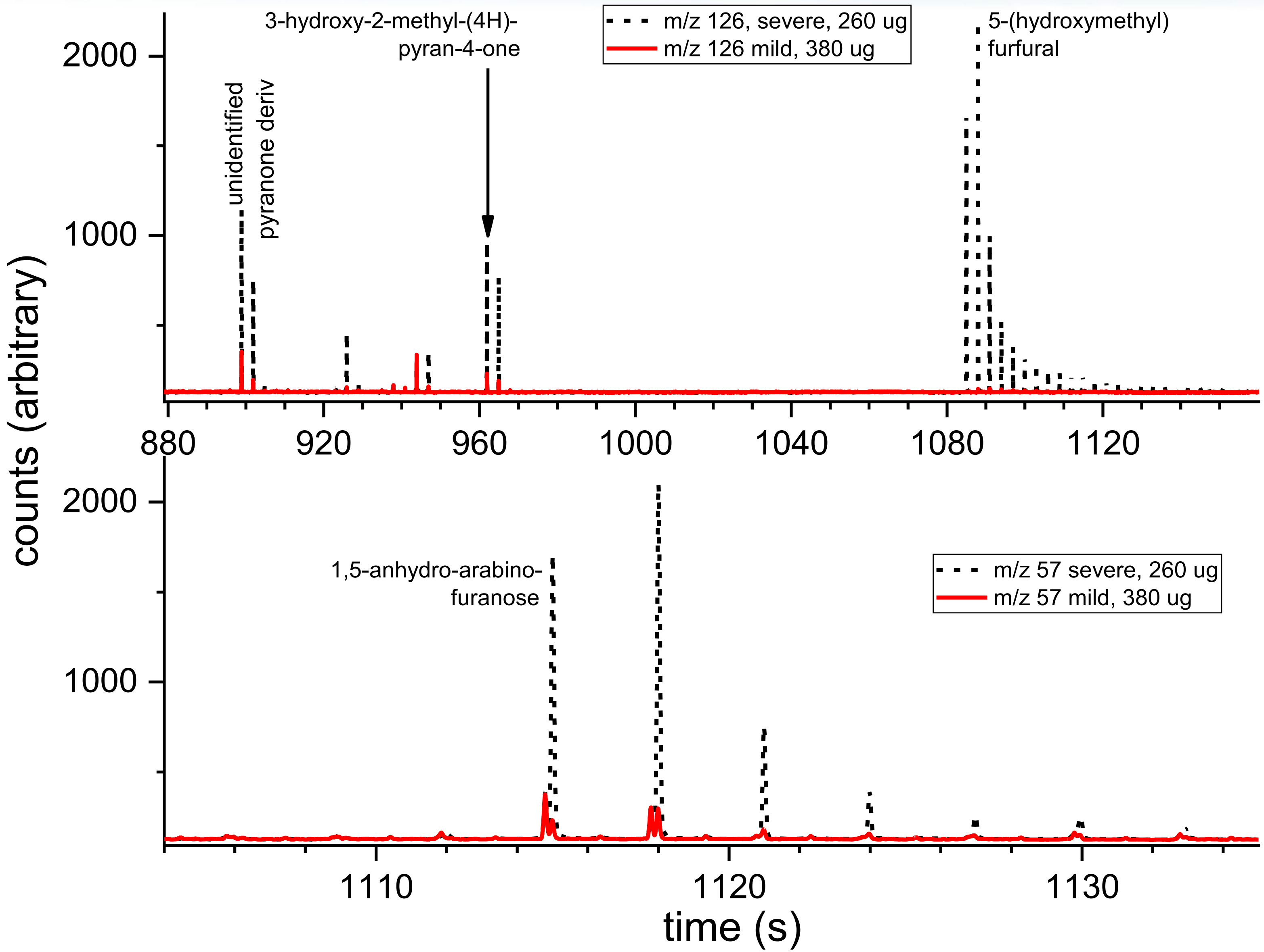
Hemicellulose Breakdown by Microbial Preprocessing

- Low temperature pyrolysis (400°C) sensitive to changes in bio- polymer structure, chemistry
- Unheated corn stover (top) shows production of 4-vinyl phenol, modest quantities of oxygenates
- Microbially heated corn stover (bottom) generates significant quantities of C4, C5 oxygenates
  - furfural and pyranone derivatives likely originating from C5 sugars (hemicellulose)
- Selective degradation of C5 sugars suggests selective microbial preprocessing is achievable



Groenewold, G. S., et al. (2020). "Signatures of Biologically Driven Hemicellulose Modification Quantified by Analytical Pyrolysis Coupled with Multidimensional Gas Chromatography Mass Spectrometry." ACS Sustainable Chemistry & Engineering **8(4): 1989-1997.** (Feb 3, 2020)

Comparison of Mild vs. Severe Heating

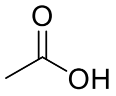


Quantitation of Production Efficiency for Oxygenates

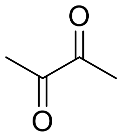
- Quantitatively compared pyrolysis production efficiency for seven commercially available oxygenates

- Pyrolysis Production Efficiency Responses can vary
  - dependent on sample mass
  - sample tube morphology

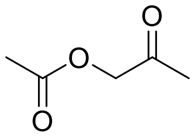
- Internal standard 9-(9H)-fluorenone used for quantitation of mass spectrometer response.
  - selected for stability under 300 ^{o}C-700 ^{o}C pyrolysis temperatures



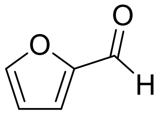
Acetic acid



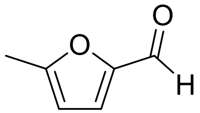
2,3-Butanedione



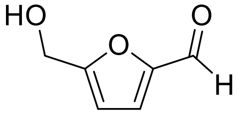
Acetoxyacetone



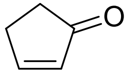
2-Furfural



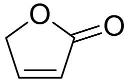
5-Methylfurfural



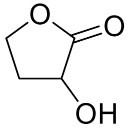
5-(Hydroxymethyl)furfural



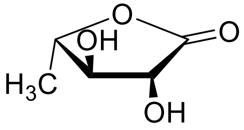
2-cyclopenten-1-one



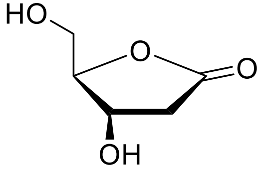
2(5H)-furanone



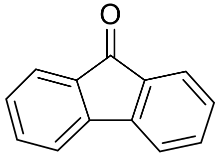
2-Hydroxy-γ-butyrolactone



5-Deoxy-L-arabino-1,4-lactone



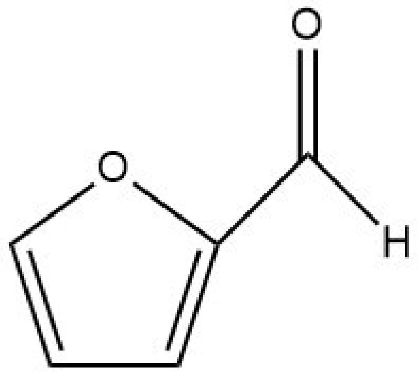
2-Deoxy-R-ribono-1,4-lactone



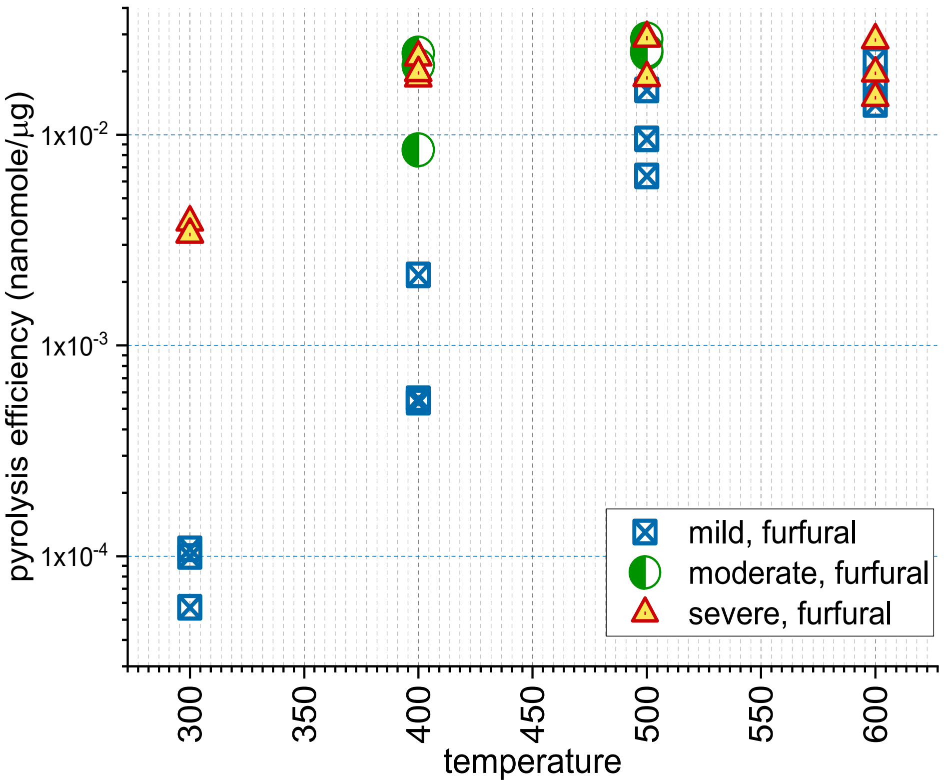
9-(9H)-Fluorenone

Effect of Temperature on Pyrolysis Efficiency

- Pyrolysis efficiency measured by quantitation using internal standard method
- Seven oxygenates exhibited changes in pyrolysis efficiencies
- Not every oxygenate exhibited pyrolysis efficiency changes
  - 2-Cyclopentenone



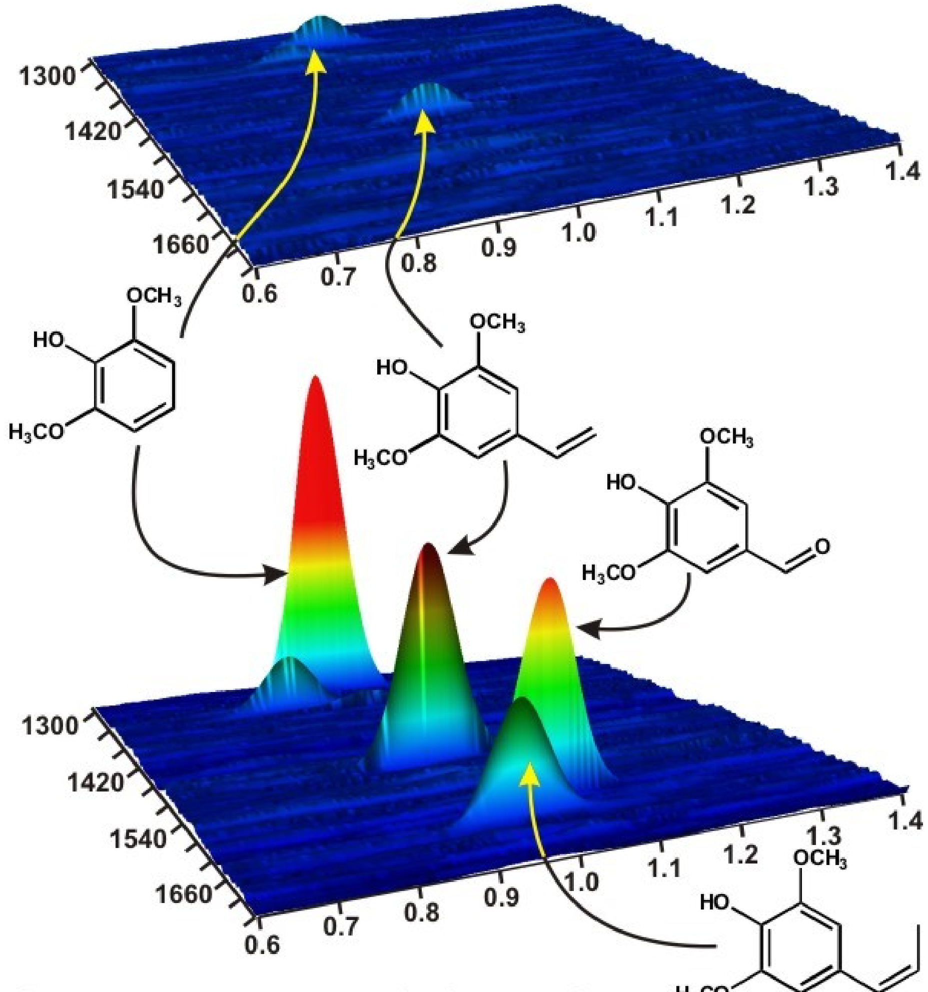
Furfural



Lignin Breakdown by Microbial Preprocessing

- New research focused on effects of microbial heating, emphasizing effects on lignin, specifically syringols
- Low temperature pyrolysis (400^{o}C)
- Mildly-heated to unheated corn stover samples show modest syringol, vinyl syringol
- Microbially heated shows 2-order enhancement, plus generation of formyl and propenyl derivatives
- Syringyl lignins thought to add to biomass rigidity
  - possible correlation to processing attributes
- Correlation with the quantity of S-lignins degraded is a significant research challenge / opportunity

Corn stover, mildly heated during storage



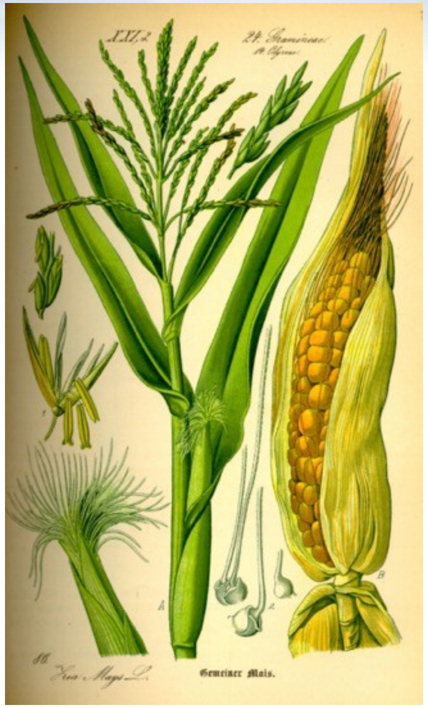
Corn stover, severely heated

Conclusions

- Molecular characterization approach to elucidate cell wall modification in biologically degraded corn stover
  - Analytical pyrolysis-GCxGC MS can provide molecular-level information when applied to biomass samples

- Temperature matters when performing molecular characterization
  - Low-temperature (400°C), analytical pyrolysis may offer improved characterization for identification of cell wall structural changes

- Enhanced understanding and management of variability to inform harvest and storage best management practices in the biomass value chain
  - Microbial activity plays an important role
    - managed to decrease biomass variability or harnessed as an intentional preprocessing technique



Characterizing Bale Degradation

Signatures of Biologically Driven Hemicellulose Modification Quantified by Analytical Pyrolysis Coupled with Multidimensional Gas Chromatography Mass Spectrometry
2020, *ACS Sus. Chem. Eng.*
https://doi.org/10.1021/acssuschemeng.9b06524

Current Knowledge Gap

- Biomass degradation during long-term storage negatively affects the conversion performance and value the biomass
- There has been limited success in quantifying degradation beyond visual inspection

Achievement

- We used py-GC/GC to identify and quantify breakdown products in corn stover samples with different biological heating/degradation profiles
- The findings suggest that biological heating disrupts the cell wall structure, fragmenting the hemicellulose or cellulose chains

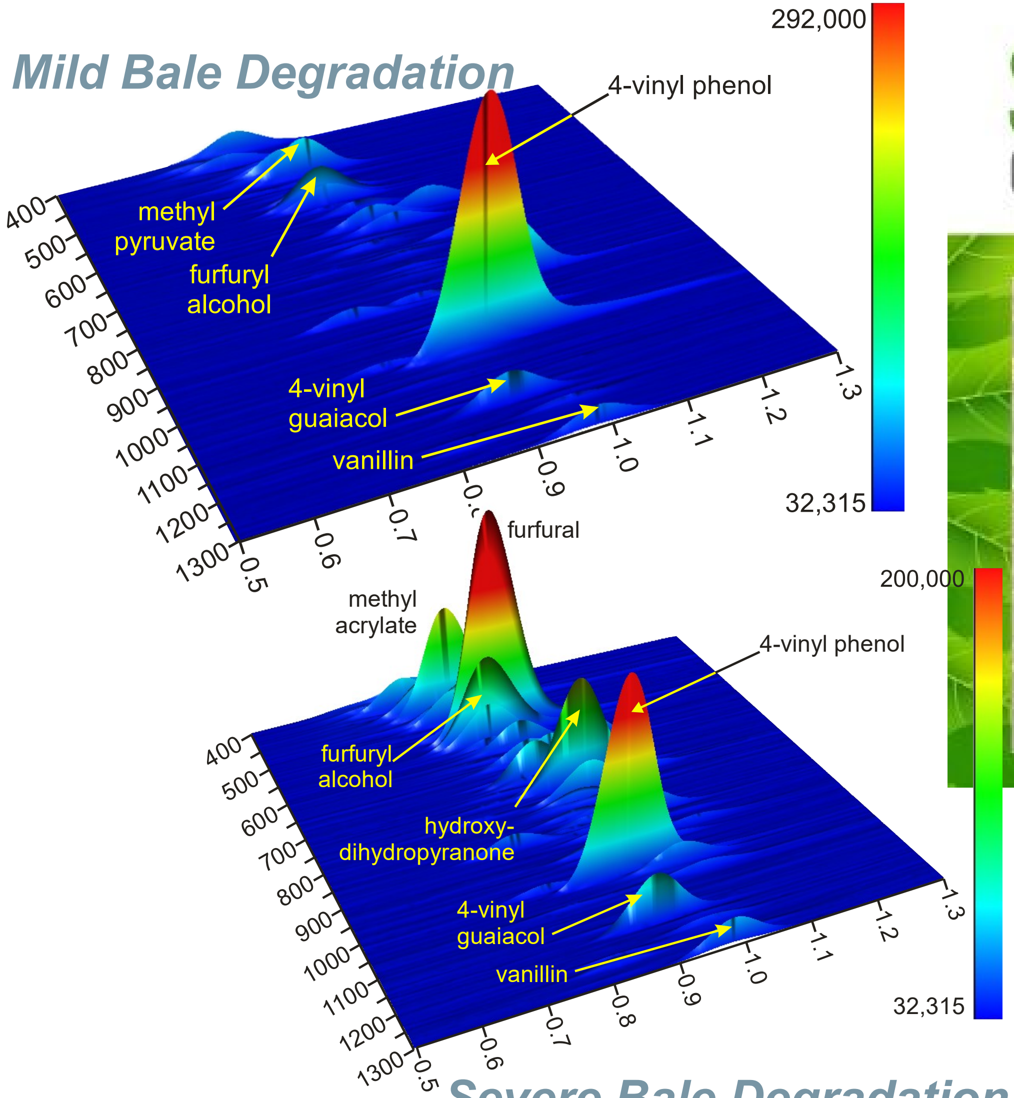
Relevance

- Stakeholders within the bioenergy industry can use this technique to rapidly characterize biomass feedstock degradation and correlate with downstream conversion performance
- FCIC researchers were invited by the py-GC/GC instrument manufacturer (LECO) to present the work in an upcoming conference (Spring 2021)

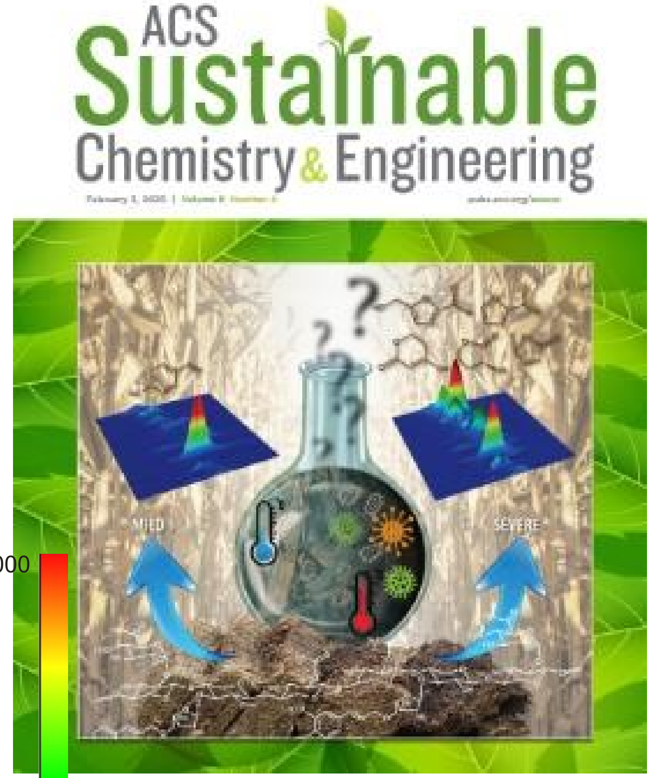
Signatures of biologically driven hemicellulose modification

- Molecular characterization approach to elucidate cell wall modification in biologically degraded corn stover.
- Low-temperature (400°C), analytical pyrolysis may offer improved characterization for identification of cell wall structural changes.
- Enhances understanding and management of variability to inform harvest and storage practices to enable the biomass value chain.

Mild Bale Degradation



Severe Bale Degradation



Groenewold et al., 2020, *ACS Sus. Chem. Eng.* https://doi.org/10.1021/acssuschemeng.9b06524

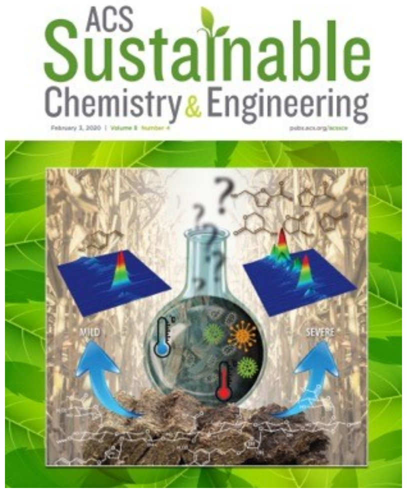
Future Directions

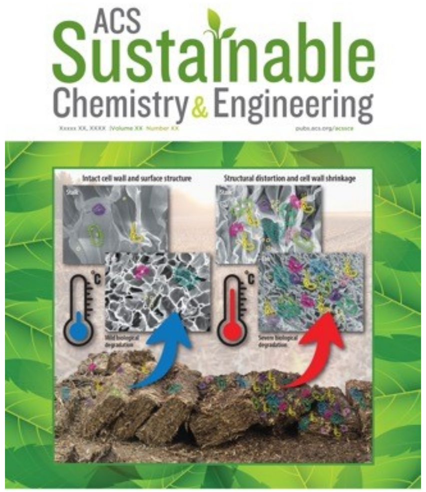
- Understand molecular impacts of variability in growth, harvest, storage, and pyrolysis conditions
  - Molecular differences between biomass feedstocks?
  - What are the effects of different pretreatment methods in biomass preprocessing?
  - How do storage conditions affect biomass feedstocks?
- Can molecular-level data be scaled up to improve industrial pyrolysis and address biomass variability?

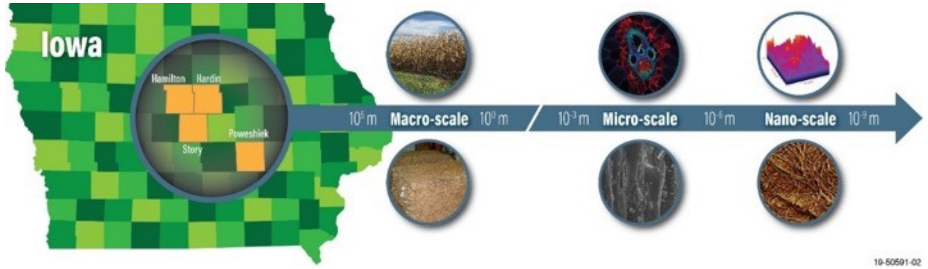
Unveiling signatures of biomass variability & biological degradation

Ensemble of papers unmask the variability of lignocellulosic biomass, submitted to *ACS Sustainable Chemistry & Engineering*

1. G. Groenewold, B. Hodges, A. Hoover, C. Li, C. Zarzana, K. Rigg, A.E. Ray, *Signatures of Biologically Driven Hemicellulose Modification Quantified by Analytical Pyrolysis Coupled with Multidimensional Gas Chromatography Mass Spectrometry*, (Feb 3, 2020 issue with cover art)
2. Leal, J., Torres, E., Rouse, W., Moore, C., Sutton, A., Hoover, A., Li, C., Resch, M., Donohoe, B., Ray, A., Semelsberger, T. *Impacts of inorganic material (total ash) on surface energy, wettability & cohesion of corn stover*.
3. Ray, A.E., Williams, C., Hoover, A., Li, C., Sale, K., Emerson, R., Klinger, J., Oksen, E., Narani, A., Yan, J., Beavers, C., Tanjore, D., Yunes, M., Bose, E., Leal, J., Bowen, J., Wolfrum, E., Resch, M., Semelsberger, T., Donohoe, B. *Multi-scale characterization of lignocellulosic biomass variability and its implications to preprocessing and conversion —a case study for corn stover*.
4. Li, C., Kerner, P., Williams, C.L., Hoover, A., Ray, A. *Characterization and Localization of Dynamic Cell Wall Structure and Inorganic Species Variability in Harvested and Stored Corn Stover Fractions as Functions of Biological Degradation*.
5. Yan, J., Oyedeji, O., Leal, J., Donohoe, B., Semelsberger, T., Li, C., Hoover, A., Sun, N., Webb, E., Bose, E., Zeng, Y., Williams, C., Schaller, K., Ray, A.*, Tanjore, D*. *Characterizing variability in lignocellulosic biomass - A review*.
6. Oyedeji, O.; Gitman, P.; Qu, J.; Webb, E., *Understanding the Impact of Lignocellulosic Biomass Variability on the Size Reduction Process: A Review*.
7. E. Bose, J.H. Leal, A.N. Hoover, Y. Zeng, C. Li, A.E. Ray, T.A. Semelsberger, and B.S. Donohoe, *Impacts of biological heating and degradation during bale storage on the surface properties of corn stover*. (Submitted to *ACS Sus Chem Eng*)





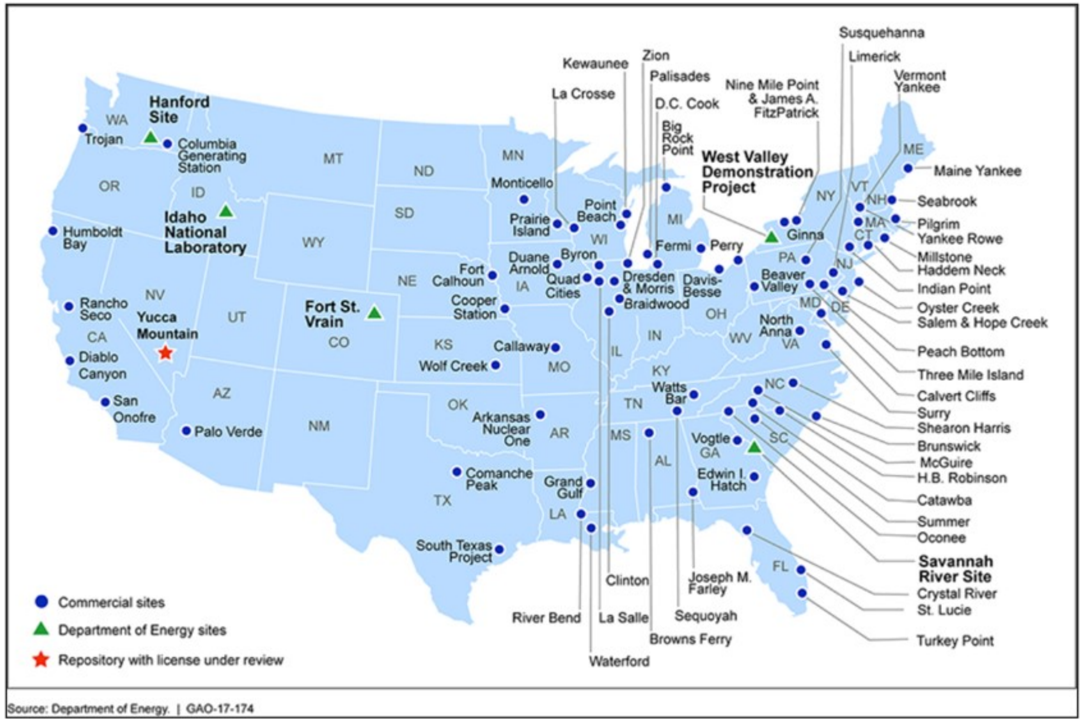


Project 2:

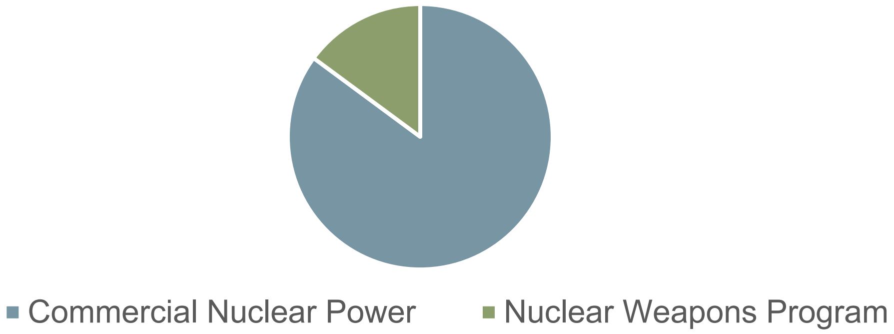
Macromolecule radiolysis with radical capping donors

Problem #1: Spent Nuclear Fuel

- Used nuclear fuel costs in the billions of dollars each year to store and manage
- USA has 90,000 metric tons of nuclear waste requires disposal
- U.S. commercial power industry generated nearly 80,000 metric tons
- Waste is stored where it was generated—at 80 sites in 35 states
- Waste expected to increase to ~ 140,000 metric tons over the next several decades. However, there is still no final disposal site in the United States



USA Nuclear Waste Sources

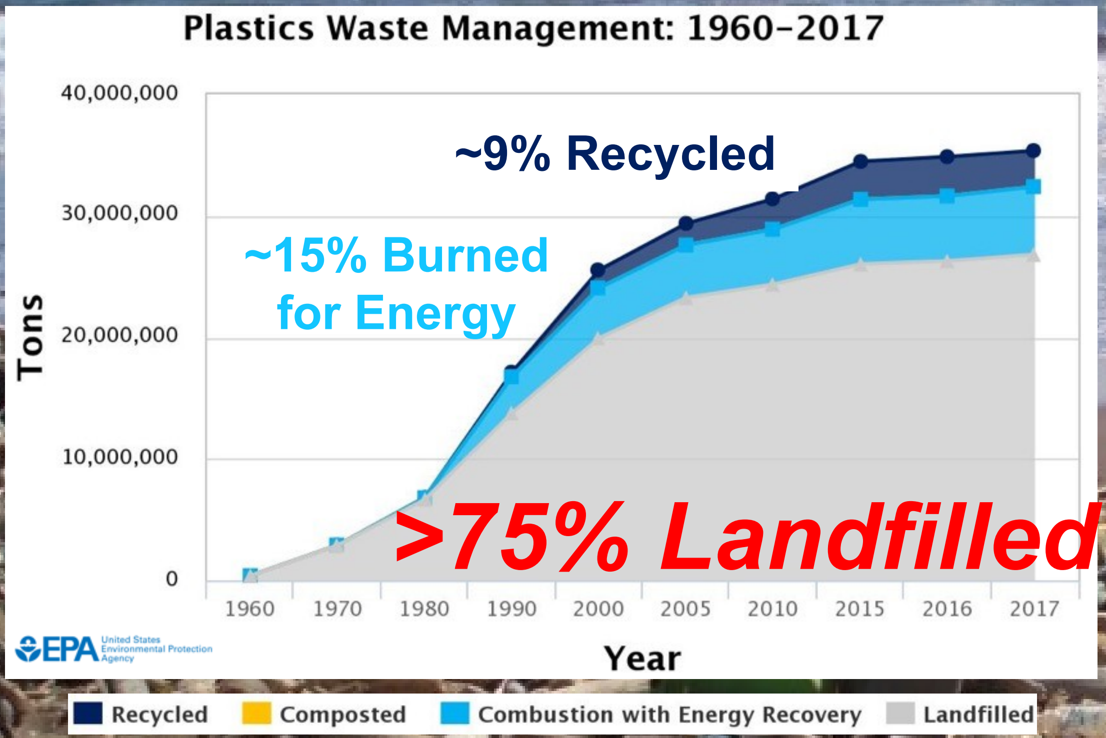


***The problem** is that the used fuel is highly radioactive*

***The opportunity** is that ionizing radiation breaks chemical bonds*

https://www.energy.gov/sites/prod/files/2017/03/f34/ISF%20Cost%20Implications_final_rev1.pdf
https://www.gao.gov/key_issues/disposal_of_highlevel_nuclear_waste/issue_summary#t=0

Recycling of Plastics Presents an Opportunity



Source: NOAA Marine Debris Program

The problem is that 150 million tons of plastic waste are generated globally per year

The opportunity is that the chemical building blocks of these polymers have value – <u>if they can be disassembled</u>

The benefit is that each ton of plastic recycled saves 130 million kJ of energy (22 barrels of oil)

~$38 billion added to U.S. economy each year.

Rahimi, A.; García, J. M., *Nature Reviews Chemistry* **2017,** *1* (6)

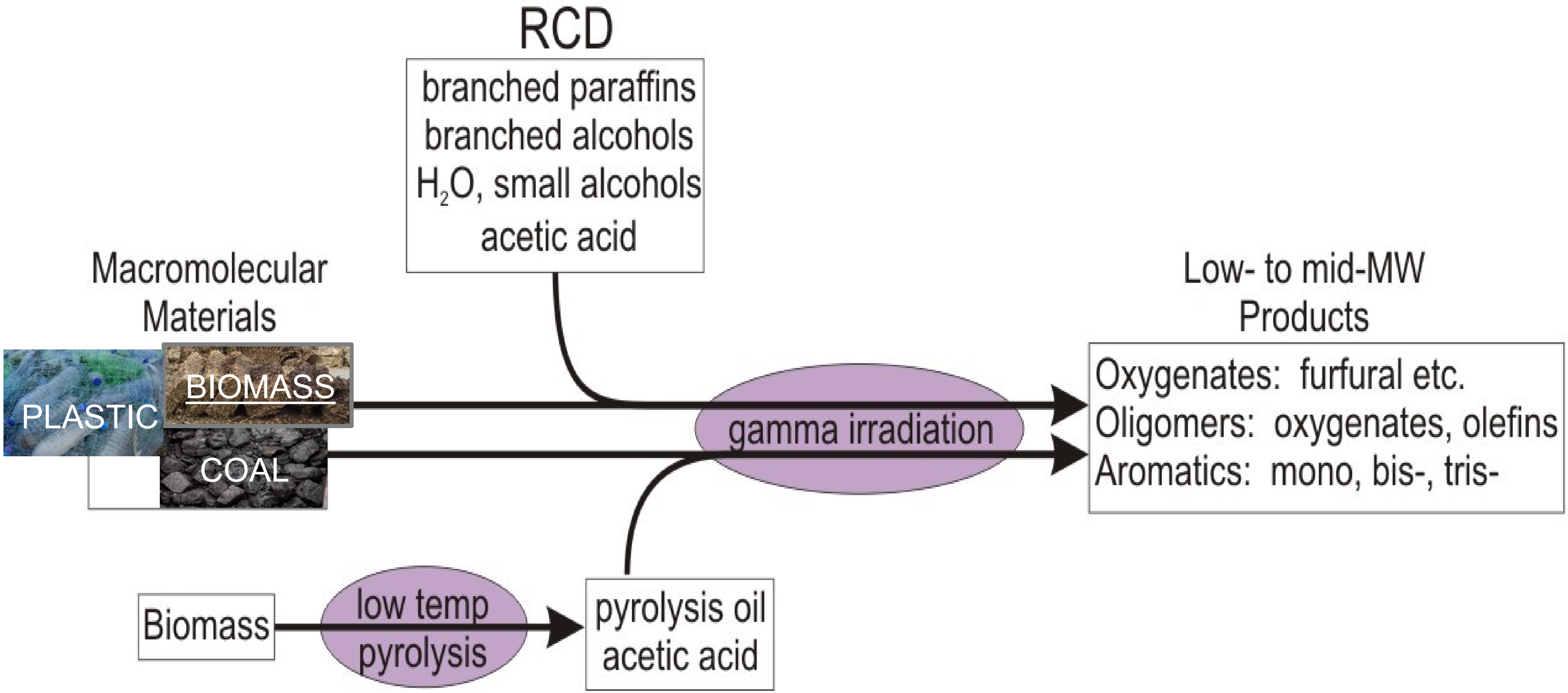
"…if they can be disassembled…" *Using Gamma Irradiation for Breaking Chemical Bonds, Moderated with a Radical Capping Strategy*

- ***The problem*** is that radiation breaks chemical bonds, forming molecules with unpaired e^- (aka, radicals)
  - Radicals formed from large molecules can recombine, forming even larger molecules (*i.e.*, making the problem worse)
- ***The approach*** is to interrupt recombination by infusing small molecules that form small radicals that will "cap" the large radicals before they recombine (*new jargon, apologies,* Radical Capping Donors or RCDs)
- ***The product*** should be lower molecular weight materials amenable to further processing or recycling

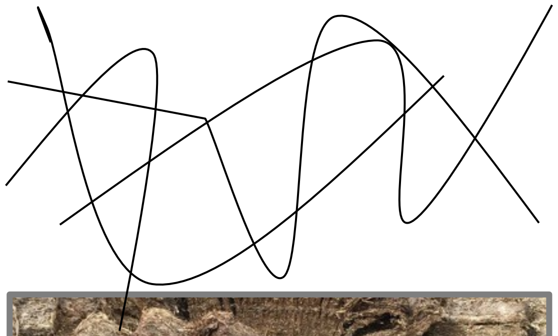
Research Plan

1. Macromolecular materials – waste plastics, biomass, coal –
    a. infused with RCDs
    b. gamma irradiated
    c. to produce lower-molecular weight chemicals that can be more easily separated.
    – Conversion chemistry can be optimized by adjusting feedstock composition, irradiation time, and choice of RCD.
2. Irradiation of a mixture of low-temperature pyrolysis oil and intact biomass, waste plastics, or coal is hypothesized to furnish low- to mid-molecular weight organics
    a. RCDs generated from py-oil

Research Plan

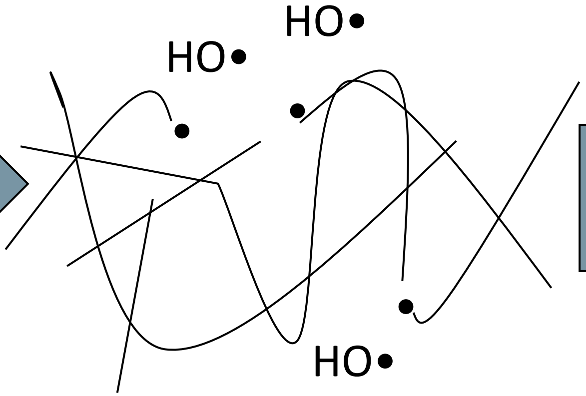


Reaction Scheme



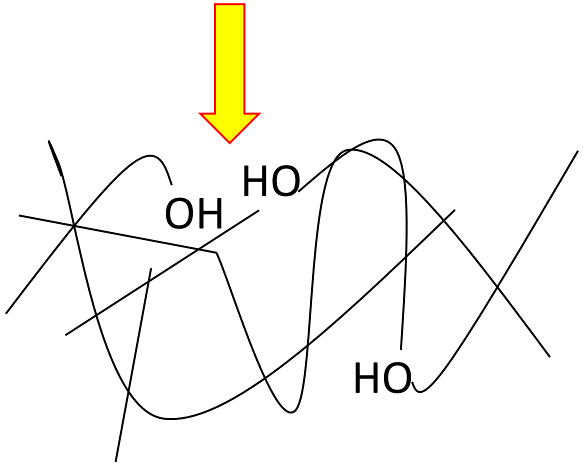
Radical Forming Species
hydrogen radical (H•)
methyl radical (H_3C•)
hydroxide radical (HO•)

GAMMA IRRADIATION



Bonds Broken; Macromolecule Radical Species of Lower Molecular Weight and Small Radicals

And, hydroxlylated or carbonylated intermediates are nutritious carbon sources for microbes!



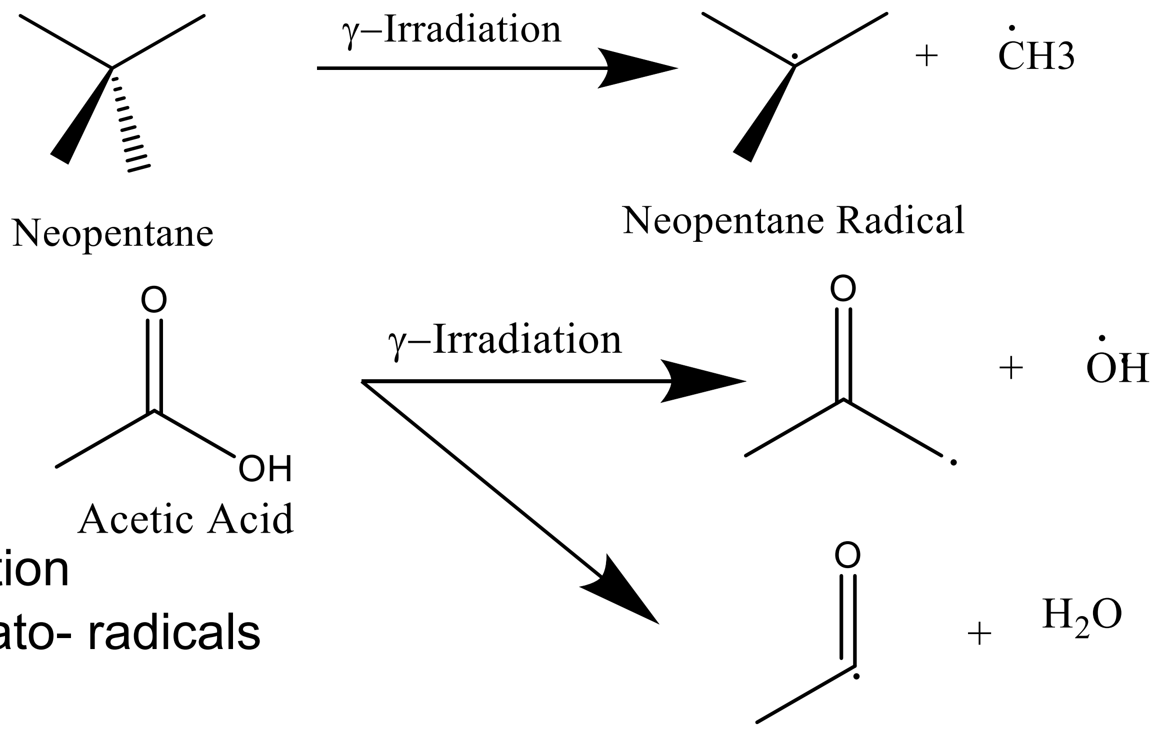
Lower Molecular Weight Chemicals That Can Be Separated by Existing Technologies

Approach: Controlled Studies Using the γ-Irradiator, leading to POP Experiments Using Spent Fuel

- Ionizing radiation coupled with radical capping strategy offers an opportunity for specific degradation that would be unlikely to occur under everyday conditions but **could be selectively produced and controlled**
- Leverage INL's extensive capability in radiation chemistry from fuel cycle programs
  - world class excellence in identification and quantification of radiolysis products
- γ-irradiator capacity
  - doubled with new instrument in EIL
- γ -tube at ATR is underutilized
  - Opportunity to use NSUF

Potential Radical Capping Reagents

- Low-molecular weight branched organic molecules with a high propensity for generating H•, H_3C• and or HO• upon irradiation.
  - Neopentane
  - Isopentane
  - Isobutane
  - Isopropyl alcohol
  - Isobutyl alcohol
  - t-butyl-alcohols
  - Acetone
  - Methyl ethyl ketone
  - Acetic and formic acids
    - H•, H_3C• and/or HO• upon irradiation
    - Ability to form keto- and carboxylato- radicals



Scientific Benefit in 3 Areas

- Industrially Relevant Chemical Transformation
  - Transforming biomass
    - preprocessing feedstock for fine chemicals
  - Converting coal
    - feedstock material useful for conversion to fine chemicals
  - Plastic recycling:
    - Depolymerization to smaller units
      - fine chemicals or recycling

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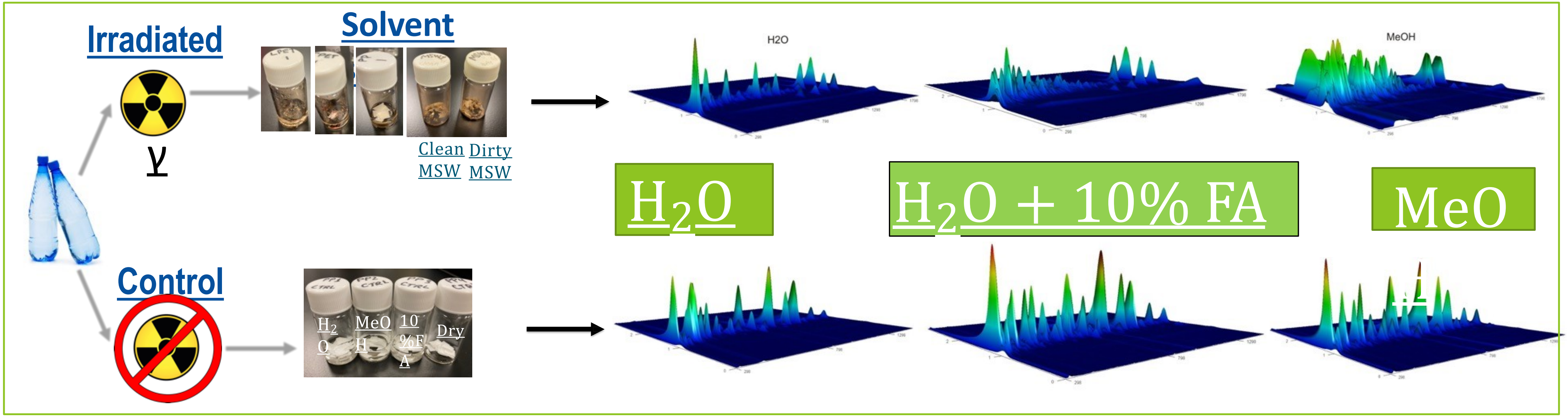
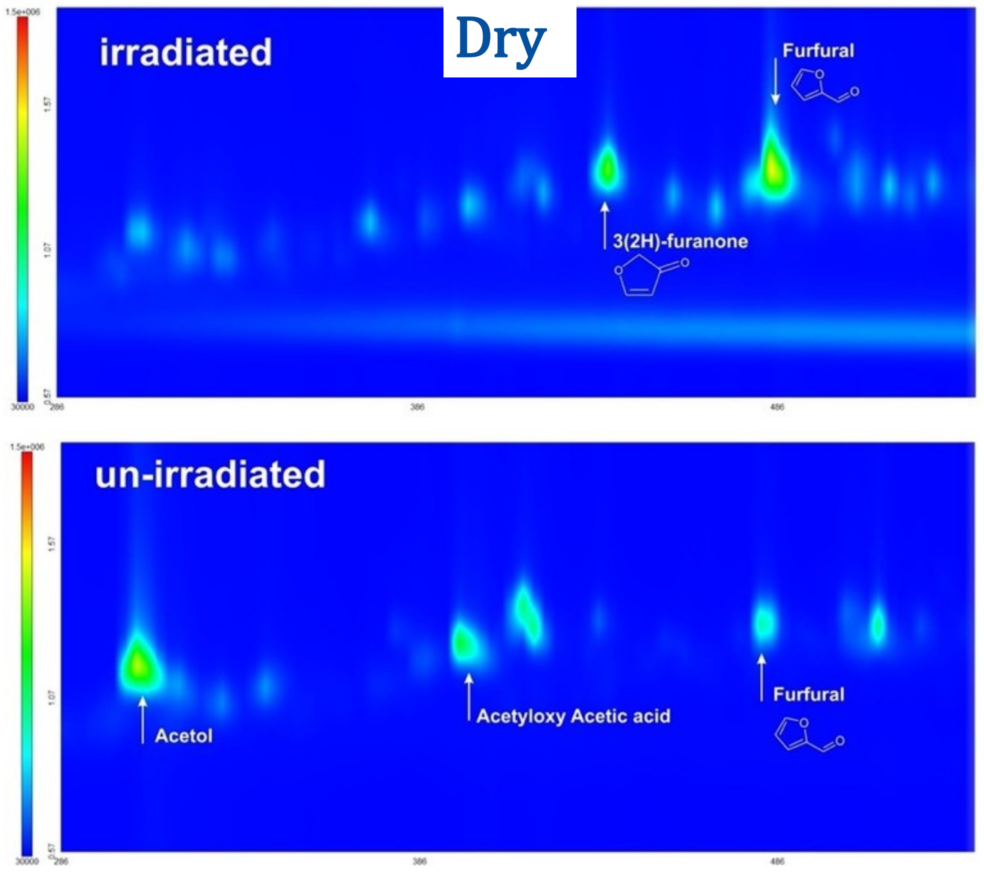
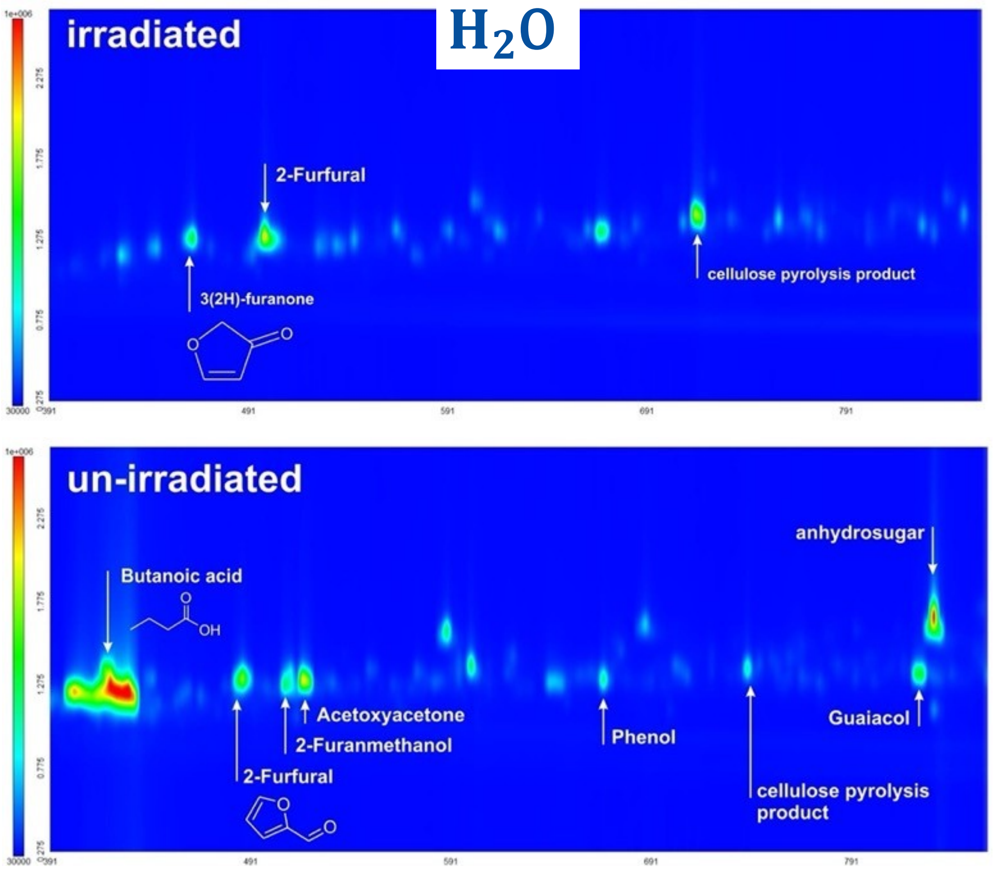
Research Approach



Irradiation of Corn Stover: Dry or Water



There are a larger number of lower-abundance peaks in the irradiated sample. (RT1: 286-550; RT2: 0.57-2)

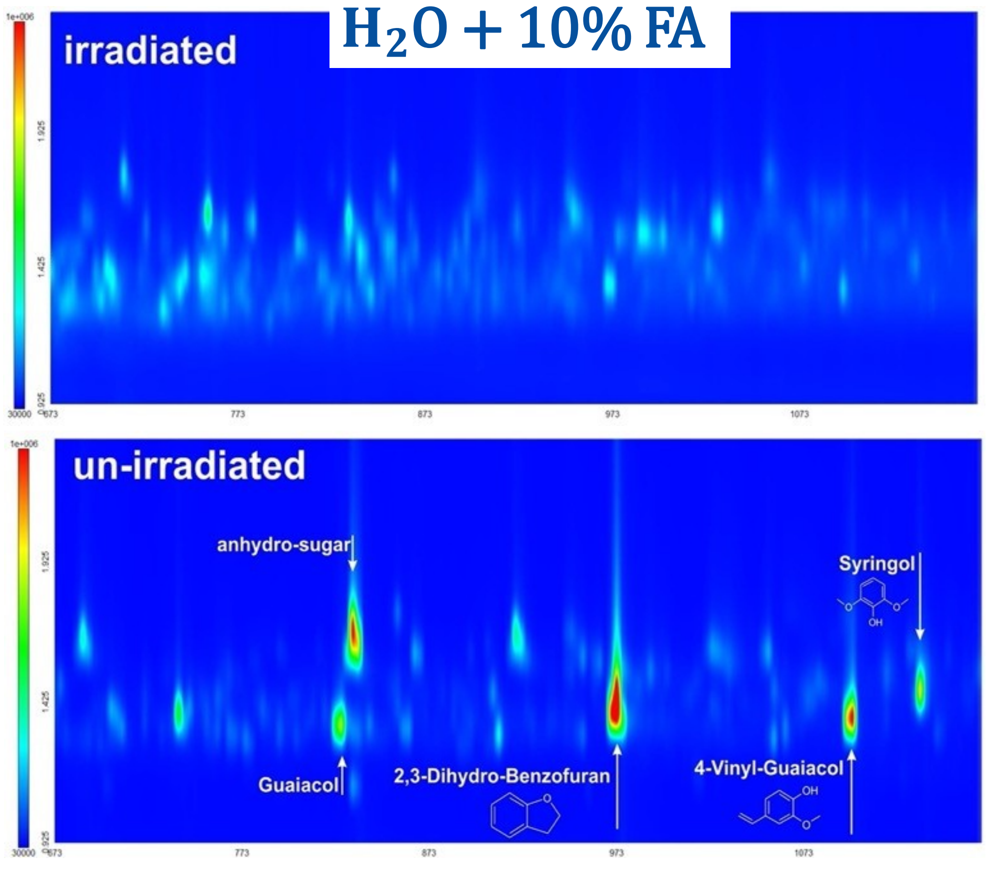


More abundant compounds like guaiacol disappear after irradiation. (RT1: 391-820; RT2: 0.275-2.5)

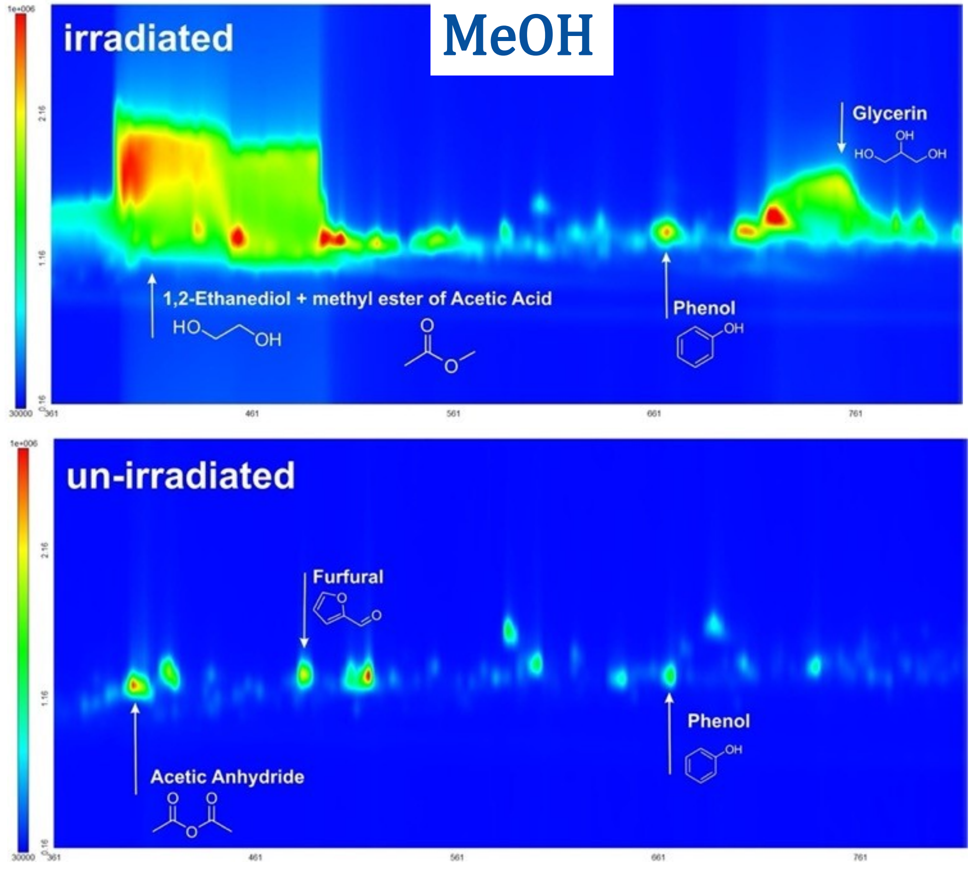
Post-Irradiation

Pre-Irradiation

Irradiation of Corn Stover: 10%Formic Acid or Methanol



The irradiated sample has a larger number of lower-abundance peaks and peaks with higher second retention times. (RT1: 673-1125; RT2: 0.925-2.25)



The difference suggests that a combination of methanol and radiation is causing the change (RT1: 361-800; RT2: 0.16- 3.16).

Post-Irradiation

Pre-Irradiation

Results

- Observed significant differences between irradiated and un-irradiated samples
- Differences between solvent conditions
- Methanol irradiation showed most significant spectral changes
- Increase in lower abundance peaks: data processing/peak identification is ongoing
- Hemicellulose and cellulose (guaiacol, syringol) tend to disappear after irradiation
- Cross-linking is occurring
- Radiation is inducing a change, both physical (density, color, texture) and chemical
- ChromaTOF Tile is a useful new software tool for analyzing complex GCxGC-MS spectra.

Conclusions

Conclusions

- Characterization of biomass variability is possible with analytical pyrolysis two dimensional gas chromatography with mass spectrometry
- The high variability of biomass requires rapid characterization efforts to make real-time decisions about feedstock choices and blending for large scale pyrolysis and biorefining
- GCxGC-MS can be one tool to characterize biomass
- Macromolecule modifications can be performed through use of ionizing radiation. We are continuing to explore this method of modifiations

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Chenlin Li, Ph.D.

Amber Hoover

Lynn Wendt

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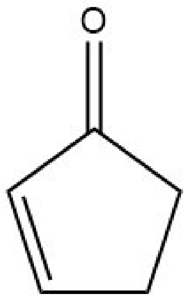
Pyrolysis Efficiency Studies In Hemicellulose Derived Oxygenates

- Seven oxygenates exhibited changes in pyrolysis efficiencies
- Not every oxygenate exhibited pyrolysis efficiency changes
  - 2-Cyclopentenone



2-Cyclopentenone